A STUDY OF COMPLEX FORMATION. IN SOLUTIONS OF THE STANNOUS HALIDES BY MEANS OF ABSORPTION SPECTRA MEASUREMENTS.

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by

HENRY JAMES WALLS, B. Sc.

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I. INTRODUCTION.

The formation of complexes and complex ions in solution, and the related phenomena of association, have long been a source of interest to chemists. With the establishment of the ideas of electrolytic dissociation, the complementary ideas of association of ions to form complexes came almost automatically into existence. Stable complex salts such as $K_4Fe(CN)_6$ have been known for a very long time, and as far back as the 1850's HITTORF (1) showed the existence of complex-formation by the union of one metallic ion with several halide ions in solutions of CdI_2 and ZnI_2.

Since the term complex formation has to cover such a wide variety of effects, it is convenient to subdivide it into:-

1. Association under the action of interionic forces into indefinite, impermanent groups;
2. formation of stable complexes of definite composition.

But these must be considered merely as limiting cases, since it is almost impossible to draw a sharp distinction. The distinction is parallel to that between homo- and hetero-polar combination. Case 2. above is now an accepted part of text-book chemistry, thanks to the work of WERNER, but case 1. is still a subject of discussion among chemists.

At the present time, we are being forced to realise that the association of ions in solution occurs more commonly than was formerly supposed. The extent of the association is largely bound up with the polar nature of the solvent, and recent research has shown that substances which are strong electrolytes in water may be weak electrolytes in less polar solvents. (2). But evidence has also accumulated which suggests that association of type 1 occurs even in aqueous solutions of typical strong electrolytes (3, 4, 5).

There is, however, one class of salts which has long been recognised as showing above all others the tendency to complex formation - viz., the halides (and cyanides) of the heavy metals of the sub-groups of the periodic table - Cu., Ag., Au., Zn., Cd., Hg., Ge., Sn., Pb., etc. A very large number of stable complex ions with these metals as central ions is known; Eg: $Ag(CN)_2^-$, $SnCl_6^{4-}$. Solutions of the halides of these metals also show numerous special properties which distinguish them from both the typical "strong" and "weak" electrolytes; these properties are to be ascribed to the tendency to complex formation. For example, the ion Hg^{++} binds Cl^- ions so strongly that $HgCl_2$ is well known to be practically undissociated even in dilute solution. Again, $PbCl_2$ while showing a higher conductivity in dilute solution than $CaCl_2$

(a "strong" electrolyte)*, yet shows, not a decreased, but an increased solubility in presence of a sufficient excess of the chloride ion (6, vol. VII, p. 714). Such examples might be greatly multiplied.

The tendency to complex formation is governed by a number of different factors and VAN ARKEL and DE BOER (7, p. 192) have summarised these very neatly. The following points, taken from their summary, are of interest in the present connection.

1. A complex is more stable, the smaller and more highly charged the central ion;

2. The greater the polarisability of both the central and the co-ordinated ions, the more stable is the complex;

3. Complexes with a kation of the sub-groups as central ion are more stable than those with a kation of the main groups in the same position.

1. is a natural consequence of the laws of electrostatics† (but see also below), and 3. has been observed (above) as an empirical fact, but polarisation effects need some more consideration.

From the work of HABER, REIS, BORN, FAJANS, and others

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* For $CaCl_2$, μ at 1/512 m. = 124.0 (6, vol. III, p. 713)
For $PbCl_2$, μ at 1/512 m. = 133.1 (6, vol. VII, p. 711).

† Assuming that, in the union of ions to form a complex, the latter is more stable the greater the decrease in potential energy during the process.

(see 10, par. 3) we must conclude that on the close approach (as in chemical union) of two ions, each of these is to a greater or less extent deformed by the electrical field of the other. A great deal of work on this theory and its implications has been done by FAJANS (8, 9, 10, 11, 12). Briefly stated, it is supposed that when a positive and a negative ion are close together, (either in a crystal of the salt concerned, or in a strong solution of it), there results a deformation of the electron systems, the negative ion tending to repel the electron system of the positive ion, and the positive ion attracting the electron system of the negative ion. Fig. I illustrates this:

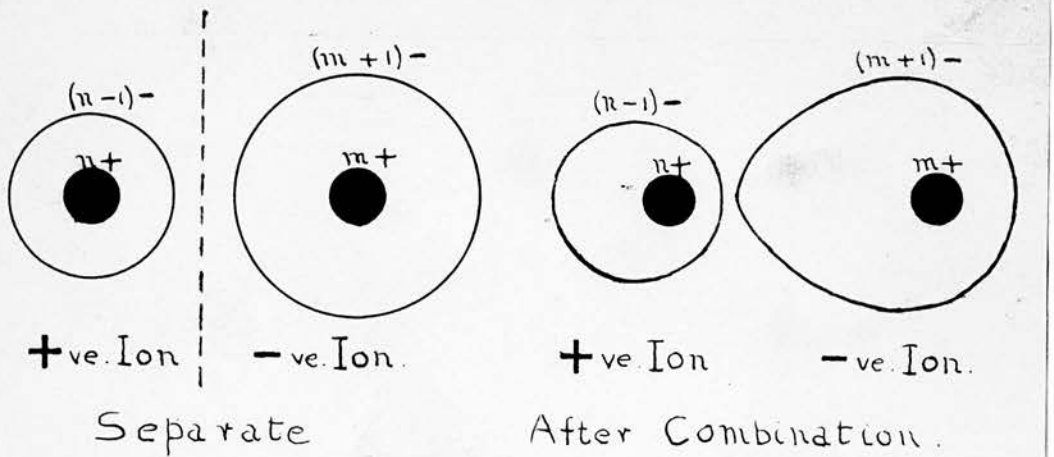

FIG. 1.

The total effect, it will be seen, is to make a theo-

retically purely heteropolar union approach more to the homopolar type, and render a sharp distinction between homo- and hetero-polar union impossible (12, par. 1). It can easily be seen that the greater the extent of the deformation, the firmer is the union between the ions. For if we suppose the deformation to succeed the coming together of the ions, it will be a spontaneous process resulting in a loss of potential energy, and the greater the extent of the deformation, the more energy lost, and the more work must be done to re-separate the ions. It is obvious that the extent of the deformation depends on the properties of the ions concerned. An ion of multiple charge will exert a greater deforming (polarising) effect than one of single charge, and a small ion will also deform more strongly on account of its more intense field; cf. point 1. above. Furthermore, the deforming effect of the kation (positive) on the anion (negative) will be much greater than the effect of the anion on the kation; i.e., an anion is much more polarisable than a kation. This is of course because (a) the electron system is very much more firmly held in the kation, on account of the excess positive charge in the nucleus, and (b) while the anion will tend to repel the electron system of the kation, thus sending it into a weaker field so that the restoring forces will balance the field strength when the deformation is

small, the kation on the other hand will attract the electron system of the anion, thus drawing it into a stronger field so that the deformation is very large before the restoring forces balance the field strength. In fact, in the majority of cases, the effects due to the polarisation of the anion are so great as to mask entirely those due to polarisation of the kation .

But there is one class of kations whose own polarisability may not be neglected: these kations, peculiar in a number of respects, are the kations without inert-gas structure, i.e., containing in most cases 18 electrons in the outer shell. A glance at the periodic table shows that these are just the kations of the heavy metals mentioned above, which are particularly strong complex-formers. - Cu., Ag., Zn., Hg., Sn., Pb., etc. It is found that these kations are both more polarisable and more strongly polarising than kations with an inert gas structure - i.e., with 8 electrons in the outer shell. For example, in the calculation of lattice energies, it is found that while the experimental and calculated values agree well for the alkali and alkaline earth halides, for the halides of the heavy metals the experimental value is always much greater than the calculated, pointing to a pronounced strengthening of the union through polarisation (7, pp. 66, 69, 77). Again, while Ag. and Na. have almost the same ionic radii FAJANS and

JOOS calculate the refractivity of the Ag. ion in the crystal lattice to be greater than that of the Na. ion in the lattice in the ratio 4.79 : 0.50, indicating an approximately ten-fold greater polarisability of the Ag. ion (9). "The difference between the lattice energies of a salt with a heavy-metal kation and one with an inert-gas kation increases also as we pass from less to more deformable anions, indicating a stronger polarising action by the heavy-metal kation". (8, par. 5). In short, kations of the heavy-metal type hold other ions more strongly than kations of the inert-gas type. VAN ARKEL and DE BOER (7, p. 172) sum this up as follows: "We find for the metal ions of the sub-groups both large polarisability and strongly polarising action. Hence the actual lattice energy is always greater than that calculated on the basis of BORN'S theory. . . . The same difference between main- and sub-groups is seen in complex formation. The energy set free by this is greater for ions of the sub-groups than is calculated from the charge and size of the central ion. Hence these complex compounds are especially stable."

Now it is natural to expect that any change in the electronic system of an atom will make itself manifest by a corresponding change in optical properties; and, furthermore, that this change will be especially marked in the case of compounds containing a heavy-metal kation. The fact that the salts of these

metals are frequently coloured is qualitative evidence for this. Also, the halides of, e.g., $Ag.^{+}$, $Hg.^{++}$, $Pb.^{++}$, $Ni.^{++}$ (none of which kations has an inert-gas structure) all show a pronounced colour-deepening as we pass from chloride to iodide, easily comprehensible when we remember that the size and hence deformability of the anions increases in the order Cl^{-} less than Br^{-} less than I^{-}.

In quantitative studies by optical methods we may use either (i) refractivity or (ii) absorption. Deformation of an electron system would naturally tend to affect the energy change between two levels, and hence the frequency of the radiation absorbed, (see 11, par. 16; 9, par. 12); dispersion theory deals with the connection between refractivity and absorption (17, p. 464; see also 13, p. 1332). The study of the refractivities of electrolytes has been especially developed by Fajans and his school. It can tell us with exactitude the degree of association (or complex formation) in solution, but little or nothing about the nature of the products. But by studying absorption spectra we get, as it were, a "third dimension" in our view of the absorbing substance. Association, or complex formation, with consequent ionic deformation will make itself directly evident by changes in absorption. "The examination of the light-absorption of salt solutions of different con-

centrations makes it possible to come to a definite conclusion about the nature of the association in solutions of electrolytes, in so far as changes in the state of chemical combination - e.g., formation of complex salts or molecules - result in considerable changes in the position and character of the absorption bands". (20).

A good deal of work, some of it of a rather empirical nature, has been done on the absorption of salts in solution. v. HALBAN and EISENBRAND (15), for example, estimated the degree of association of the alkali nitrates from absorption spectra measurements. But from what has been said above, it would naturally be expected that the effects on absorption of complex formation, etc., should be most pronounced in the case of the heavy metal halides, where a strong tendency to complex formation goes hand in hand with a large degree of polarisation. And this is actually found to be the case. SCHEIBE (14) ascribes the peculiar form of the absorption spectrum of the iodides of Hg., Cd., Zn. in alcoholic solution to complexes and undissociated molecules; while FROMHERZ, in a more systematic series of researches, has found that (a) the absorptions of solutions of the alkali (17) and alkaline earth (18) halides show practically no change with change of concentration, as might be expected from the small polarisation and small tendency to complex for-

mation with these salts, and (b) in solutions of the halides of the heavy metals Cu., Ag. (16), Pb., Tl. (19), Hg., Cd.,(20; this paper summarises all work down to summer of 1931) quite new absorption bands, ascribable to neither the kation nor the halide ion, appear, and the position and height of these bands varies with changes of concentration and with changes in the ratio $\frac{[\text{Halide ion}]}{[\text{Metallic ion}]}$. These bands are to be ascribed to complexes.

The research in the case of the lead halides (19) having yielded a number of valuable and interesting results,on the formation of, nature of, and equilibrium among lead - halogen complexes, it was felt desirable to carry out a similar investigation of the closely related stannous halides, and this research is now described below.

II. PREVIOUS WORK ON THE SUBJECT.

In 1889 ENGEL (21), studying the solubilities of some metallic chlorides in HCl, found that in the case of some of these, including $SnCl_2$, as the concentration of HCl increased, the solubility of the chloride first fell, passed through a minimum, then rose to a value much exceeding that in pure water. He says, "this action seems to be chemical and to arise in the formation, in the body of the liquid, of definite compounds of HCl with the chlorides". In the case of $SnCl_2$ he claims to have isolated one of these, as a solution corresponding to $SnCl_2$, HCl, $3H_2O$, yielded when frozen crystals of identical composition.

YOUNG later went more deeply into this question (22). He found that for solutions of SnI_2 in HI (i) the solubility as compared with that in water decreases with increasing amounts of HI up to a concentration of HI of 7%, then increases, and, with more than 25% of HI exceeds that in water; (ii) in HI of concentration greater than 25%, the SnI_2 solubility curve has a reversed temperature gradient below about 30° C. Hence he concluded that a "new system", stable at low temperatures, and more soluable than SnI_2, was present in the system. He succeeded in isolating an unstable compound, which analysis by indirect methods showed to have the composition $HSnI_3$. He later (23)

published an investigation of "The Electrical conductivity of Solutions of $SnCl_2$ in HCl". In these solutions the conductivity decreases with increasing concentration of HCl; this evidently points to complex formation decreasing the number of ions present. Various details led YOUNG to the conclusion that two different complexes (e.g., $HSnCl_3$, H_2SnCl_4) were present. He also tried the effect of replacing the HCl in part by KCl and by KI. For equivalent amounts of KI and HCl, KI produced a much bigger decrease in conductivity, which he attributed to the (expected) greater stability of $KSnI_3$ than of $KSnCl_3$. NOYES (24), reporting on the above work, observed that since YOUNG's results show that the decrease in conductivity is proportional to (i) $[H^+][Cl^-]$ and (ii) $[SnCl_2]$, this is evidence that $SnCl_3^-$ is the chief association product in concentrated solution, and not $SnCl_3^-$ and $SnCl_4^{--}$ together, as YOUNG had suggested.

YOUNG's results were confirmed by an independent method by GOLDSCHMIDT (25, 26). GOLDSCHMIDT found that in the reduction of nitro-compounds by $SnCl_2$ in presence of HCl, the reaction velocity was given by

$$v = K. [R.NO_2] [SnCl_2] [HCl].$$

This shows that a complex is the active reducing agent: If the reduction had been effected by $SnCl_2$, then v would have been independent of $[HCl]$, and if the reduction had gone according to the equation

$R.NO_2 + SnCl_2 \quad 2\,HCl = R.NO + H_2O + SnCl_4$ *

v would have been proportional to $[HCl]^2$. Hence the active complex was apparently the simplest possible one, $SnCl_3^-$. This agreed with NOYES' view. GOLDSCHMIDT also found that stannous bromide in hydrobromic acid reduced the nitro-compound about eight times as fast as $SnCl_2 + HCl$, a fact which could not be explained were Sn^{++} the active agent, while it was quite reasonable to assume that $SnCl_3^-$ and $SnBr_3^-$ might not be equally active.

Finally, twenty-five years later, PRYTZ, starting from GOLDSCHMIDT's results, undertook to determine exactly the nature and concentrations of these complexes (27). She determined the normal potential for Sn/Sn^{++}, and then made a series of measurements of E. M. F.'s at a tin electrode in solutions of stannous halides containing increasing concentrations of the halide ion; this gave the decrease in the activity of Sn^{++} with increasing concentration of halide ion, thus providing a measure of the complex formation. It is unnecessary to describe PRYTZ's calculations in detail, but a table of her results is appended;

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* A nitroso-compound was definitely shown to be the first product of reduction.

TABLE I.

Percentage of tin present as various complexes:-

A. $SnCl_2$; Concentration of $SnCl_2$ = 0.01 molar throughout.

Concentration Cl^-	0.01m.	0.1m	1.0m	3 molar
Sn	80.5	30.0	1.6	0.1
SnCl	18.7	52.3	21.8	4.4
$SnCl_2$	0.8	16.6	43.7	23.4
$SnCl_3^-$	0	1.1	26.4	42.5
$SnCl_4^{--}$	0	0	6.5	29.6
"Bound" Cl per Sn.	0.20	0.89	2.14	2.97

B. $SnBr_2$; Concentration of $SnBr_2$ = 0.01 molar throughout.

Concentration Br^-	0.01m	0.1m	1.0m	3 molar
Sn	91.1	52.0	4.7	0.45
SnBr	8.6	36.7	25.9	7.05
$SnBr_2$	0.3	10.8	48.0	39.4
$SnBr_3^-$	0	0.5	21.4	53.1
$SnBr_4^{--}$	-	-	-	-
"Bound" Br per Sn.	0.09	0.60	1.86	2.45

PRYTZ also calculates conductivities and finds results agreeing fairly well with YOUNG's (23).

In two recent papers (28), WALTON and his co-workers confirmed GOLDSCHMIDT's conclusions that a complex is the effective reducing agent in stannous chloride solutions. They find that in the oxidation of stannous chloride in solution by air, the rate of oxidation is greatly increased by increasing the Cl^- concentration; e.g., for the same concentrations of tin, it is thirteen times as great in 7N HCl as in 0.45N HCl. They conclude that "in the aut-oxidation of $SnCl_2$ there is reason to believe that a complex chloro-acid is the form in which the Sn^{++} is oxidised".

There seems to have been no previous work on the absorption spectra of stannous halides, beyond an observation by DROSSBACH (29) that a solution of stannous chloride (a 20mm. layer of 10% solution) absorbs radiation of wavelength less than 340mμ.

III. GENERAL PLAN OF WORK.

With the above general considerations and previous results in mind and guided by the previous work on the lead halides (19), it is now possible to outline a scheme of work on the stannous halides. In a solution containing metallic ions M^{++} and halide ions Hal^- the absorption should be obtainable by the addition of the absorptions of M^{++}, Hal^-, and any complexes present. Conversely subtracting the absorptions due to M^{++} and Hal^-, in so far as these ions are present, from the total measured absorption should give the absorption due to any complex or complexes present. Hence a complete investigation demands a knowledge of the absorption of (i) M^{++}, (ii) Hal^-, (iii) solutions containing M^{++} and Hal^- in varying proportions.

The absorption of the halide ions Cl^-, Br^-, I^- is already known from previous work (13, 14, 17, 18). As in the case of Pb^{++}, the absorption due to Sn^{++} should be obtainable through measurements on $Sn(ClO_4)_2$, as the ClO_4^- ion does not itself absorb above 200mμ (31), and no association or complex formation is to be expected here, on account of the very small polarisibility of the already complex ClO_4^- ion (11, par. 9d).

Solutions containing varying proportions of metallic and halide ions were obtained in the case of the lead halides by using solutions of the pure lead

halide in water at concentrations varying from saturated to about 1/1000 saturated, and then solutions of the same containing excess of the corresponding alkali (generally potassium) halide in a ratio $\frac{[K\ Hal]}{[Pb\ Hal_2]}$ of about 6000. A generally similar method of work is applicable in the case of the stannous halides, but the following points of difference must be borne in mind:

1. the stannous halides are much more soluble, and hence measurements are possible over a larger range of concentration, but

2. the stannous halides are hydrolysed in dilute solution, hence, except in very concentrated solution, an excess of halide ion must always be present.

The well-known sensitivity of the Sn^{++} ion to oxidation by the air must also be borne in mind; i.e., the solutions must be protected from the atmosphere as far as possible.

In the second part of the work below it is sought to extend our information by measurements on tin halides in non-aqueous (alcoholic) and aqueous-alcoholic solutions. On account of the large influence which the nature of the solvent has on electrolytic dissociation, we might expect to observe different degrees or sorts of complex-formation in different solvents.

IV. METHODS OF MEASUREMENT.

(a) General Remarks

By the term "absorption spectrum", used in a quantitative sense, is usually meant the curve showing the variation of the "absorption coefficient" with the wavelength (or frequency). The absorption coefficient is defined by the BEER-LAMBERT Law for the absorption of light by an absorbing medium;

$$I = I_o e^{-\epsilon c d} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{or} \qquad \log_e \frac{I_o}{I} = \epsilon\, c d \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here I_o is the intensity of the beam of monochromatic light.

I is the intensity of the same beam after passing through a length, d, of the absorbing medium.

C is the concentration of the absorbing substance.

ϵ is the absorption coefficient.

In practice, d is expressed in centimetres, c in mols per litre, and the more convenient $\log s_{10}$ are used instead of $\log s_e$. This gives a different absolute value of the absorption coefficient, in this case denoted by k, where $k = 0.4343\epsilon$. Hence the determination of an "absorption spectrum" involves the measurement of values of k corresponding to a number of different wavelengths spaced at small intervals.*

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*In plotting the absorption curve, log k is generally used in place of k, as, since the values of k measured may vary between, say, 10^{-1} and 10^{5}, in this way features in the curve occuring at widely different values of k are more equally brought out.

A few words on the physical implications of the BEER-LAMBERT law might be added. The law may be divided into two parts:

(1) $\log \frac{I_o}{I} \propto d$ (Lambert's law).

(2) $\log \frac{I_o}{I} \propto c$ (Beer's law).

With properly conducted measurements, and in the absence of any photochemical change, LAMBERT's law is found to be universally true. This shows that the validity of the BEER-LAMBERT law does not depend on the absolute light intensity (32). For, if it did, the absorption at the "back" of a thick layer would follow a different law from that governing the absorption at the "back" of a thin layer, and LAMBERT's law would not then hold.

BEER's law deals with individual molecules, and it means that each molecule has an individual absorption independent of its distance from the others. In all that follows, the validity of BEER's law is a fundamental assumption, as it is taken for granted that the absorption curve of any definite ion in solution will show no change in height (value of k) or position of maximum (value of λ) over all the range of concentration examined. I.e., any change in an absorption curve with concentration is assumed to be evidence for a corresponding change in the nature and concentration of the absorbing ion or ions present.

BEER's law has received abundant experimental verification (32); it holds absolutely, within the limits of experimental error, at small concentrations, and only at large concentrations are small deviations from it found. This is quite understandable when we remember that at small concentrations the absorbing molecules will not be able to influence one another, but that as the concentration increases and they approach close to one another polarisation effects, as discussed in section I, will appear. v. HALBAN and EBERT (32) find deviations from BEER's law for the ion NO_3^- at concentrations greater than m/1, and according to WEIGERT (33) the complex ions $Cr_2O_7^{--}$, CrO_4^{--}, MnO_4^-, $PtCl_6^{--}$ etc. show similar deviations at high concentrations. However, in almost all of the solutions measured in this work the concentrations of the absorbing substance were small and in the region of complete validity of BER's law. And in any case, the deviations which do appear are small; for example, the relatively polarisable halide ions show only a very small change in absorption with change in concentration (17).

Actually to measure k, it would theoretically be simplest to pass a beam of light of known wavelength and known intensity through a known thickness of a known concentration of the absorbing substance, and to measure the intensity of the emergent beam.

This is the method used by v. HALBAN and SIEDENTOPF (34) who used a monochromator and a photo-electric cell and reached an accuracy of 0.1%. But if k is to be measured for a large number of different wavelengths the method becomes exceedingly slow and laborious, and a photographic method is enormously more convenient. In this, two exactly similar, (i.e., of equal I_0,) beams of light are passed through a spectrograph and their images caused to fall side by side on the plate. One beam passes through the absorbing medium, and the intensity* of the other reduced to a known extent, i.e., so that its I_0/I is determinate. To compensate for any absorption of the first beam by the containing tube and solvent, an exactly similar tube containing only the pure solvent is generally introduced into the path of the second beam. On the plate the spectrum of the first beam will show greater blackening than the "comparison spectrum" in the region of free transmission, but less blackening in the region of absorption; at some wave-length the two spectra will show exactly equal blackening, i.e., I, and hence I_0/I, is equal for the two beams. Hence, C† and d having been fixed, k

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* or the time of exposure, which is considered equivalent. But see below.

† C is, of course, the concentration of the complex-forming substance: e.g., where a solution contains both $SnHal_2$ and KHal, C is the concentration of $SnHal_2$.

is easily found using the equation:

$$\log k = \log (\log I_o/I) - \log c - \log d \quad . \quad . \quad . \quad (3).$$

Using various values of I_o/I in the "comparison spectrum" will give different pairs of values for k and wavelength. It might be added that some writers (e.g., 35) have thought it necessary to state as an underlying assumption of the above method that "light intensities of the same wavelength are equal when they produce equal blackenings on adjacent areas of the same photographic plate in the same time". This is known as Hartmann's Principle and seems to be almost axiomatic. The use of the photographic plate introduces a slight possible error in choosing the points of equal intensity, as the smallest difference between two light intensities which an ordinary photographic plate will show as a variation in blackening is 3- 4% (36). On the other hand, the method has the following advantages:

1- It can be used over a wide range of wavelengths (λ = 200 - 600mμ with ordinary plates);

2- it can be used over a large range of absolute light intensities:

3- it permits of rapid measurements, which is useful if the absorbing substance is liable to photochemical decomposition.

For the reduction of the intensity of the comparison spectrum a number of different methods have

been proposed and used. To mention the more important of these, HOUSTON (37) and SCHAEFFER (38) used two similar light sources and varied the intensity of the illumination from one by altering its position; WINTHER (39) used a calibrated blackened gauze for the reduction of intensity; v. HENRI (40) used two equal sources and varied the time of exposure to one; JUDD LEWIS (41) used a single source, splitting a beam from it into two equal parts, and reducing the intensity of one by a series of "shutters"; and finally, a number of workers e.g., HILGER (42) and SCHEIBE (43) have used a rotating sector for reducing the intensity of the "comparison beam", which method is free from the fairly obvious objections to each of the above methods.

But on the other hand, the use of a rotating sector, and also of HENRI's method, is complicated by certain peculiarities in behaviour of the photographic plate (44, 45). Contrary to what might be expected, if two different exposure-times (t) and intensities (I) are chosen so that

$$I_1 \, t_1 = I_2 \, t_2$$

the effect on the plate is not necessarily the same in the two cases. In general

$$\frac{I_1}{I_2} = \left(\frac{t_2}{t_1}\right)^p$$

Where p is the "Schwarzschild constant", which only

exceptionally = 1. Also, intermittent illumination, as given by a rotating sector, does not necessarily have the same action as the same aggregate time of continuous illumination. Hence objections have been raised against reductions in exposure-time by the use of a rotating sector or otherwise, in place of reductions in intensity (e.g., KELLNER, 46, DAVIS 47). On the other hand, several workers, in comparative investigations on the different methods of measuring absorption spectra, have found that under the correct conditions of use, perfectly satisfactory results are obtained by the use of a rotating sector; i.e., under these conditions, Schwarzschild's constant = 1. (see ROSSLER, 44; LEY and VOLBERT, 35; BALY 45). In the HILGER (42) type of apparatus, two sectors are used, one with a fixed opening in the path of the "absorbed beam" and one with a variable opening in the path of the "comparison beam", so that the "periodicity" of the illumination is the same for both beams. HOWE (48, see also 45), using an apparatus of this type, found that "the photographic plate, the use of which in photometric work is usually regarded as questionable, integrates intermittent exposures in such a way that the comparison of two intensities can be made directly in terms of sector openings, provided that the time from the beginning to the end of the exposures is the same and that the two exposures produce an equal blackening

of the plate".

We may conclude, then, that the use of a sector involves no error likely to increase appreciably the inherent experimental error of this photographic method.

(b) Description of Apparatus Employed.

In view of the above it was decided to use a rotating sector, on account of its convenience, accuracy, and flexibility in use. In the work described below, two different sets of apparatus were used.

1. The source of light was a spark between iron electrodes. A current of 5 amperes from a 220 volt D.C. supply was passed through a mercury interrupter and induction coil, and in the secondary circuit was inserted the spark gap, condensed by two medium-sized Leyden jars. The gap for the actual light source was about 1mm., and another spark gap of about 8 - 12mm. was used in series with this. For the spectral region 200 - 205mμ, ferro-tungsten (90%W) electrodes were used for the light source. The spectrograph was a quartz instrument by Schmidt and Haensch, giving the spectrum from 200mμ to the red on a plate 15 x 30 cm. The arrangement of the apparatus was as described in FROMHERZ (49), with one modification: the use of a quartz rhombus to produce two similar beams was given up, as it made exposures in the region 200 - 210mμ inconveniently long. Instead the exposures for the

"absorption" and "comparison" spectra were made successively, the sector being interposed in the path of the light in the latter case, and the total exposure times were made exactly equal by the use of a stop-watch. The sucess of this procedure depended on the spark running very constantly, which it had been found to do. A brief outline of the apparatus, as described in (49), and procedure may be given.

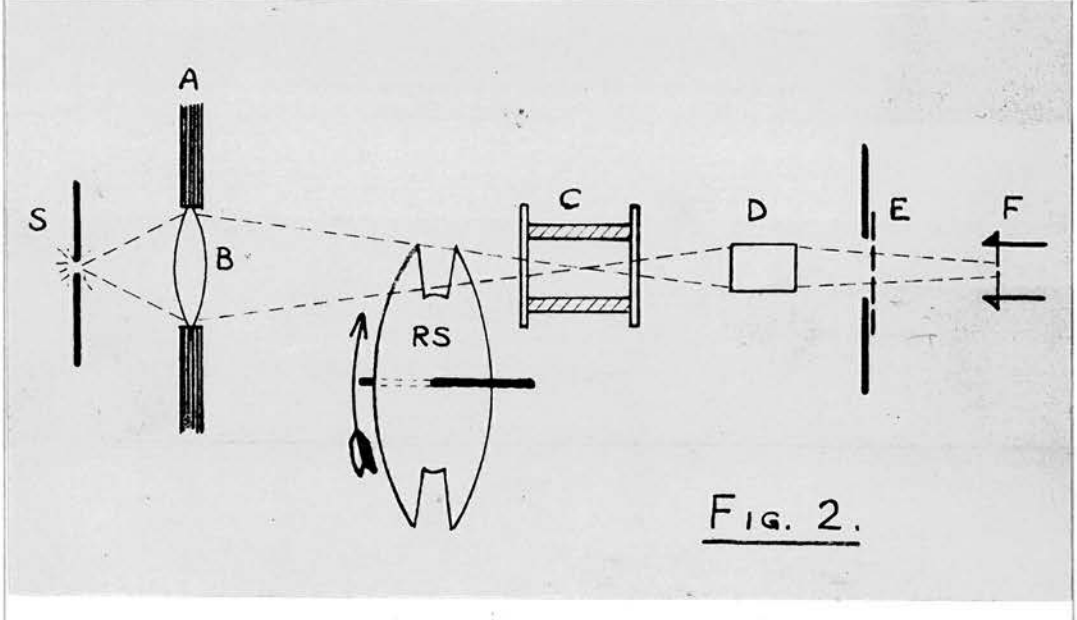

FIG. 2.

The optical system, consisting of biconvex quartz lens B and the small quartz condenser D, produced an evenly illuminated circle of light just covering the slit, F, of the spectrograph. The optical system had been arranged to give the maximum intensity of illumination of the slit. A is a sound-proof

ventilated cabinet enclosing the spark; RS is the rotating sector, which could be set for any opening up to 110°; reading directly to 0.1° on a vernier; C is the tube containing the solution (or the pure solvent, as the case may be); and E is a photographic shutter, for regulating the exposures. Exposures through the absorbing solution without the sector, and through the solvent using the sector were made alternately. To make sure that the condenser D was properly centred, it was tested from time to time by placing a lamp in the camera of the spectrograph, covering the lens B with a piece of paper, and observing whether the image of the slit was thrown exactly on to the centre of this. To minimise errors in timing, 10 seconds was the shortest exposure-time used. Exposures varied from 10 seconds with a slit of 0.03 cm. when using large sector openings and working in the region 230mμ - visible, to 5 minutes with a slit of 0.15 cm. for small sector openings and in the region of 200mμ. Fast (about 500 H. and D.) non-colour sensitive plates (both "Agfa" and "Perutz") were used. For the region 200 - 220mμ these were sensitized before exposure with oil (ordinary colourless bicycle oil, rubbed on in a thin film with cotton wool). The oil was removed before developement with acetone. A hydroquinone developer was used.

The cells containing the solution and solvent

were of two kinds: (a) for layers 0.1 - 25 cm. These were simply glass tubes clamped between crystal quartz end-plates. (Cells and mounting described in 49, par. III 4, and fig. 5), and (b) for layers 0.0001 - 0.025 cm. These were special form of "Microkuvette" supplied by Zeiss. (Cells and mounting described in 16, par. III d, and fig. 1). Their form is shown in fig. 3. To fill them a drop of the solution is placed on B, and A lowered on to this, so that the solution fills the space d, and the surplus goes into the annular channel. The thickness of layer (at d) is correct when A and B are in optical contact round the edge,

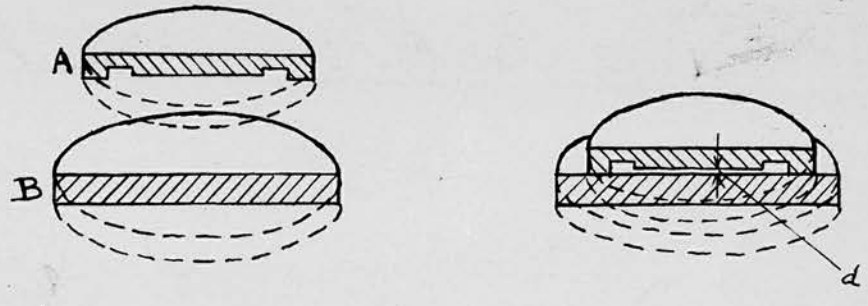

FIG. 3.

so that A is pressed on to B till the Newton's rings seen round the edge disappear. It requires a good deal of practice to accomplish this satisfactorily, and without getting liquid in between A and B at the edge; if this happens the cell must be refilled.

Before each set of exposures, an approximate calculation showed the correct value of d to use with the concentration in question. Each sector-opening corresponds to a certain value of log kcd (equation 2); e.g., for an opening of 18°, $I_0/I = 360/18x2$, (2 is present in the denominator because the sector is symmetrical about a diameter, with two openings opposite one another), and therefore $\log_{10}(I_0/I) = 1 = kcd$. Hence a table was drawn up, giving the values of log kcd for each sector-opening and also log kc for each combination of opening and size of cell. Hence log k by equation (3). The sector-openings used were chosen so as to give values of log k differing by about 0.1.

The finished plates were examined under a low-power (x8) binocular microscope in order to determine the points of equal blackening for each pair of spectra. The wavelengths were fixed by comparison with an enlarged photograph of the iron spark spectrum with the wavelengths of the lines marked. Each plate was examined twice at least, with an interval of time in between, and it was also found advantageous to reverse the plate between examinations, thus as it were,

exchanging the position of the right and left eyes: when this led to two different points being chosen, a mean position was taken.

2. In the second part of the work using non-aqueous solvents, a different apparatus was used, namely a Bellingham and Stanley sector photometer in conjunction with a Bellingham and Stanley "medium" quartz spectrograph (taking a 10 x 4 inch plate). This combination gave the spectrum from about 205mμ to the red. An iron spark 2 - 3mm. in length was used as before, in series with a second spark gap, and in parallel with a condenser of about 0.025 microfarad capacity. The spark was worked by a transformer on the 230 volt A.C. supply, giving about 6000 volts across the secondary. No special optical system was necessary, but as the cells of the photometer were mounted on convergent axes, the spark had to be at the intersection of these; a latitude in its position of a few mm. each way was allowable. When the spark was in the correct position, the fact that the two cells had identical "entrance pupils" determined that two exactly equal beams should be produced. The photometer had two sectors, one with fixed and one with variable opening; the latter read directly in terms of log I_o/I, giving values of this quantity of 0 to 2. A range of cell sizes of 0.1 to 4.0cm. was available- cells with screw-on ends for 1.0, to 2.0 and 4.0cm., and glass distance-pieces with quartz endplates for 0.1, 0.2 and 0.4cm. These thicknesses

in the latter case were not quite accurate, but accurate measurement with a micrometer enabled a corrected value of log d to be fixed. It was found not advisable to use values of log I_o/I less than about 0.15, as then the two spectra of the pair were of such nearly equal intensity in the region of no absorption, that it was very difficult to fix the point of equal blackening. The exposures which did not, of course, need to be timed with accuracy, were rather longer than with the other apparatus, especially as the solvents used usually showed a slight absorption themselves in the farther ultra-violet (less than 230mμ). No oiling of the plates was found necessary for wavelengths greater than 210mμ. Ilford "Thin-film Halftone" plates were used for wavelengths less than 400mμ and were very satisfactory on account of their high contrast; but as they were most insensitive to longer wavelengths, "Zenith Super-Sensitive" (650 H.and D.) plates were used for this region.

As a binocular microscope was not available, the plates were merely examined with a magnifying glass. This was quite satisfactory. A new Wavelength scale was prepared by photographing the arc and spark spectra of Fe side by side, using a Hartmann diaphragm, and taking the wavelengths from photographs of the arc spectrum issued by HILGER.

Other details of manipulation should be mentioned. With aqueous solutions, the water in the solvent cell (re-distilled over $KMnO_4$) was degassed under the pump before use, as otherwise bubbles tended to form inside the end plate of the cell. As all stannous solutions are very sensitive to atmospheric oxidation, the filling of the cells, etc., was done under CO_2. CO_2 was passed into a large wide jar, and the bottles of solution opened, and the cells filled by means of pipettes, in this jar. Further CO_2 was passed into the bottles before re-stoppering them. This method of working was found quite satisfactory even for $Sn(ClO_4)_2$, (see below) which is oxidised with extraordinary rapidity when exposed to the air.

V. MEASUREMENTS IN AQUEOUS SOLUTION.

(a) Preparation of Substances: Methods of Analysis.

$Sn(ClO_4)_2$:- This was prepared by the method of NOYES and TOABE (50). CuO (KAHLBAUM's "zur Analyse") was dissolved in 30% $HClO_4$ (MERCK's "garantiert rein") by warming on the steam bath. When no more CuO would dissolve the excess was filtered off, a few mils $HClO_4$ added to destroy any basic salt, the solution evaporated to small volume, and the $Cu(ClO_4)_2$ which crystallised out on cooling filtered off at the pump. After two recrystallisations from water, a solution of 65 grammes of the pure product in 100 mils. oxygen-free water was then brought on to 30 grammes granulated Sn (MERCK's "garantiert rein") under an atmosphere of CO_2, and the solution kept under CO_2 till it had become colourless, then for a further two days. The resulting solution of $Sn(ClO_4)_2$ (about 2 molar) was pipetted off under CO_2 into a number of small (15 mil.) bottles, each of which contained a small piece of tin, was filled to the neck, and was sealed with paraffin wax. Contrary to what NOYES and TOABE observed, this solution remained quite colourless.

$SnCl_2$:- For "No. 1" MERCK's "garantiert rein" $SnCl_2 . 2H_2O$ was used. Fur "No.2", granulated tin (MERCK's "garantiert rein") was dissolved in pure con-

centrated HCl to give an approximately 5 molar solution of $SnCl_2$, which was kept over excess tin.

$SnBr_2$:- 80 grammes granulated tin (MERCK's, as above) was heated with 250 grammes 40% HBr (MERCK's "garantiert rein", 1.38) for several days, till evolution of H_2 ceased. The solution was then evaporated to about one third of its volume, cooled, and the yellow crystals which separated filtered off and dried in a vacuum dessicator. The partially dry salt was heated in a small flask in a stream of CO_2, and after the evolution of water and HBr had ceased, it melted to a golden yellow liquid. The mass when cool, was recrystallised from aqueous HBr as dilute as would give a clear solution, and the crystals dried in a vacuum dessicator. Melting point 230° (uncorrected). KENDALL (51) gives 232°.

SnI_2 :- was prepared by the double decomposition of $SnCl_2$ and KI, each in concentrated (about 5 molar) solution. As recommended by KÖHNLEIN (52), only ½ equivalent of KI was used. The precipitated SnI_2 was filtered off by suction, washed with several successive small quantities of water*, and dried in a vacuum dessicator.

K_2SnCl_6 :- A colourless sample of "pink salt" (K_2SnCl_6) was used; it gave a very slightly turbid

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* The SnI_2 was probably not washed until entirely free of $SnCl_2$, but it could not be thoroughly washed, on account of hydrolysis. Attempts to recrystallise it from non-aqueous solvents were not successful.

solution, which cleared on standing.

KCl, KBr, KI:- were all MERCK's "garantiert rein". As KI in concentrated solution is sensitive to light and air, a stock solution was kept in a brown bottle under nitrogen, and delivered by a stream of nitrogen.

HCl :- was the ordinary "pure concentrated" which had been found satisfactory for this work.

HBr :- was MERCK's "garantiert rein", 1.38. (i.e., about 40%, or 6 molar).

All solutions were made up with distilled water redistilled over $KMnO_4$. The working solutions were made up volumetrically from concentrated stock solutions of the stannous halide, and the water, acid etc. $SnCl_2$ was kept as a concentrated aqueous solution, about 2.5 molar; $SnBr_2$ as a solution in HBr, both $SnBr_2$ and HBr being each about molar. In the case of SnI_2 however, as this salt is barely soluble in water and is hydrolysed by it, the solid was dissolved in KI solution as required.

As a check against possible oxidation, each working solution was generally analysed separately for its Sn^{++} content. This invariably gave a value several per cent. lower than that calculated from the amount of concentrated solution used. The analyses were carried out by means of standard iodine and sodium thiosulphate solutions. To hinder the action of any free oxygen present as far as possible, 2 drops of 1% $SbCl_3$ were added to each solution to be titrated

(53, vol. II, p. 393), and the iodine solution was measured out first, and the stannous solution then pipetted directly into the iodine. For the more dilute solutions, an approximately 0.01N solution of iodine and a similar solution of sodium thiosulphate delivered from a micro-burette were used; and this may be considered sound practice, as HÖLTJE (54) has shown that very small quantities of Sn can be determined by this means. The halide concentrations were determined volumetrically by means of silver nitrate and ammonium thiocyanate. Where the solution to be analysed contained much stannous tin this was oxidised with concentrated HNO_3 before the addition of the silver nitrate solution, as otherwise the reduction of the precipitated silver halide by the stannous tin introduced an error; a separate experiment showed that up to 50% HNO_3 in the solution introduced no error in the precipitation of the silver halide.

(b) Solutions Measured.

Table 2 summarises all the aqueous solutions measured , and gives the figure in which the absorption curve of each solution is shown.

The concentration of certain of the dilute solutions was not determined as above, but merely calculated from the volume of concentrated solution used: in these cases the concentrations given are enclosed in brackets and are probably somewhat too high. In

TABLE 2.

No. of Soln.	Description	Concentrations in Mols/litre.	Total Halide Ion concn.	$\frac{[\text{Halide Ion}]}{[\text{Sn}]}$	Curve in Fig.
1	$Sn(ClO_4)_2$ in 70% $HClO_4$	Sn 0.0977; $HClO_4$ about 8.4	----- -----	----- -----	VI
2	do.	Sn 0.106 $HClO_4$ about 8.4			VI
3	$SnCl_2$ (No.1) in water	$SnCl_2$ 2.63	2.63x2 = 5.26	2	I
4	$SnCl_2$ (No.2) in HCl	Sn 1.375 HCl 2.280	5.030	3.74	I
5	$SnCl_2$ (No.1) in HCl	Sn 0.262 HCl 0.055	0.579	2.21	I
	do				
6	do.	Sn (0.244) HCl 0.881	1.369	(5.61)	I
7	do.	Sn 0.0753 HCl 7.484	7.635	101	II
8	do.	Sn (0.0259) HCl 0.0447	0.0965	(3.73)	I
9	do.	Sn 0.00869 HCl 1.497	1.527	176	II
10	$SnCl_2$ (No.2) in KCl soln.	Sn 0.0148 KCl 3.624	3.674	248	II
11	$SnCl_2$ (No.2) in KCl HCl	Sn 0.00553 KCl 1.632 HCl 0.520	2.163	391	II
12	$SnCl_2$ (No.1) in KCl HCl	Sn (0.00533) KCl 3.77	3.94	739	II
13	$SnCl_2$ (No.2) in KCl HCl	Sn 0.00214 KCl 0.726 HCl 0.340	1.074	502	II
14	K_2SnCl_6 in water	Sn(as SnO_2) 0.612	----	---	VI
15	K_2SnCl_6 in HCl	Sn 0.00490 HCl 3.54	----	---	VI

TABLE 2. (cont.)

No. of Soln.	Description	Concentrations in Mols/litre.	Total Halide Ion conc.	$\frac{[\text{Halide Ion}]}{[\text{Sn}]}$	Curve in Fig.
16	do.(15 diluted 1:10).	Sn 0.000490 HCl 0.354	-----	---	VI
17	$SnBr_2$ in HBr	Sn 0.993 HBr 1.54	3.51	3.53	III
18	do.	Sn 0.395 HBr 0.946	1.742	4.41	III
19	do.	Sn 0.080 HBr 0.328	0.488	6.10	III
20	do.	Sn (0.008) HBr 0.159	0.175	(21.8)	III
21	do.(20 diluted 1:10)	Sn (0.0008) HBr 0.0159	0.0175	(21.8)	III
22	do.(20 diluted 1:100)	Sn (0.00008) HBr 0.00159	0.00175	(21.8)	III
23	do.	Sn 0.0981 HBr 6.351	6.549	66.6	IV
24	do.	Sn 0.0141 HBr 1.349	1.377	97.7	IV
25	do.	Sn 0.00322 HBr 0.270	0.276	85.7	IV
26	$SnBr_2$ in KBr soln HBr	Sn 0.0878 KBr 3.636 HBr 0.099	3.933	44.8	IV
28	do.(26 diluted 1:10)	Sn (0.00878) KBr 0.364 HBr 0.010	0.393	(44.8)	IV
29	do.	Sn 0.0173 KBr 3.631 HBr 0.544	4.210	243.4	IV
30	do. (29 diluted 1:2)	Sn (0.00865) KBr 1.816 HBr 0.272	2.105	(243.4)	IV

TABLE 2. (cont.)

No. of Soln.	Description	Concentrations in mols/litre.		Total		Curve in Fig.
31	SnI_2 in KI soln.	Sn	0.0175	2.785	159	V
32	do.	Sn	0.0027	1.320	487	V
33	do.	Sn	0.00246	0.754	306	V
34	do.	Sn	0.00101	0.350	347	V
35	do.	Sn	0.00043	0.276	638	V
36	do.	Sn	0.000211	6.073	28770	V

table 2, the symbol "Sn" in the column headed "concentrations" refers to the concentration of stannous tin except in the case of solutions 14, 15, and 16, where it refers to the concentration of stannic tin. The concentrations of HCl and KCl given were derived from the amount added in making the solution; the total halide concentration was determined separately for the concentrated solutions, and by calculation in those prepared by dilution. Where this latter quantity does not (as it theoretically should) equal the sum of the concentrations of the other halides plus twice the tin concentration, this indicates that a certain amount of oxidation has taken place. (But see below for the stannous iodide solutions).

It was not possible, as in the case of the lead halides (19) simply to dilute the more concentrated solutions 1:2, 1:5, 1:10 etc., and make further measurements on the diluted solutions, as, apart from the difficulty mentioned above, dilution of the solutions used here resulted in most cases in hydrolysis, and more of the halogen acid had to be added. The hydrolysis did not always take place at once, but was sometimes apparent only after several days.

It is unfortunate (see below) that the absorption of pure $Sn(ClO_4)_2$ in water could not be measured; but as the curve of a solution of $Sn(ClO_4)_2$ in 30% $HClO_4$ (not reproduced) indicated by its shape a considerable degree of hydrolysis even in acid of this con-

centration, attention was confined to solutions in the most concentrated $HClO_4$ obtainable (Numbers 1 and 2).

Number 3 was the concentrated"stock solution" of $SnCl_2$. Numbers 4, 5, and 8 contain in each case the minimum amount of HCl to give a clear (unhydrolysed) solution; Number 5, in standing some days became hydrolysed, and number 6 represents this solution after the precipitate had been redissolved in HCl.

Solution number 14 was merely a concentrated aqueous solution of the "pink salt"; as only the ion $SnCl_6^{--}$ was of importance, the concentration given represents the tin content determined by precipitation, ignition and weighing as SnO_2. On dilution, the solution threw down a precipitate, and addition of enough HCl to redissolve this gave solution number 15.

Number 17 was the concentrated "stock solution" of $SnBr_2$, and solutions 19 - 22 all contain the minimum amounts of HBr necessary to give a clear solution. Numbers 19 - 22 represent successive tenfold dilutions, but the concentrations given are probably too high. The same applies to numbers 28 (26 diluted 1:10) and 30 (29 diluted 1:2).

All the solutions of SnI_2 were made by dissolving the solid in KI solution. There was always a certain amount of precipitate formed (hydrolysis), so the clear solutions were analysed in each case for stannous tin and iodide. Hence the concentrations

given under "total halide" in table 2 for solutions 31 - 36 represent the KI plus any HI formed by hydrolysis. The use of HI solution to make the solutions, or to clear hydrolysed solutions, was avoided, as it is so easily decomposed by ultra-violet radiation. Certain difficulties which arose in the measurement of numbers 31 - 35 were probably due to the presence of HI formed by hydrolysis. It was found, especially when using thin layers of the liquid, that bubbles of gas appeared, and if left would grow so large as to occupy the entire central portion (see figure 3) of the cell. Normally, the cell had of course to be refilled as soon as the bubbles appeared. Further, subsequent examination of the plate showed that obvious large errors in the position of absorption appeared along with the bubbles. This is best explained by assuming decomposition of the HI into H_2 and I_2; the H_2 would appear as bubbles, and the I_2 would react with the stannous tin, thus altering the absorption. The curves for solutions 31 - 36 were actually obtained by refilling the cells after every two or three exposures when using the thinner layers.

VI. DISCUSSION OF RESULTS OF ABOVE MEASUREMENTS.

The absorptions of the aqueous solutions measured are shown in figures I - VI. (Hereafter, in referring to any curve, "3 II" means curve 3, figure II, and so on). Figures I - VII are tracings of the original graphs; using this scale, and ordinary squared paper, they could be plotted to the values of λ and of log k of 0.1mμ and 0.002 respectively.

(a) Stannous Perchlorate:-

The absorption curve for this (1,2 VI) has not the same simple form as the curve for $Pb(ClO_4)_2$, (19). Instead, it shows a distinct maximum at about 213mμ (log k = about 3.02), and indications of another maximum at about 235mμ (log = about 2.46). As features in the curves occurring at wavelengths less than about 215mμ are not always easy to identify on the plates, the peculiar form shown by the curve for solution 1 (1, VI) was considered as perhaps due to some experimental error; but this could hardly be the case as a fresh solution (no. 2) showed an almost identical absorption curve 2, VI .

It is obviously not possible to say with certainty where the absorption of the stanno-ion lies, but since the maxima for the simple heavy metal ions so far as measured (19), a comunication from Dr. Fromherz, generally lie round about a value log k = about 3·2 – 4·0 it is probable that the upper portions of 1 and 2, VI rising

towards 200mμ represent the long - wavelength branch of the stanno-ion absorption curve, and that the curve will reach a maximum somewhere about 185mμ .

In spite of the small tendency of the ClO_4^- ion to take part in complex formation, on account of its small polarisibility (11, par. 9d), it is probable that the maxima at 213mμ and 235mμ represent tin - ClO_4^- complexes, but it is impossible to say anything as to the nature of these.* The small size of the stanno-ion compared with the Pb^{++} ion (Sn^{++} has 32 electrons less) will of course favour complex-formation in accordance with the conceptions set forth in the introduction.

Even if we assume the upper part of curves 1 and 2,VI to represent the absorption of the pure stanno-ion, it is impossible to construct a log k - λ curve for the ion, as, owing to the unknown extent of the assumed complex formation, the concentration of the simple stanno-ion in these solutions is also unknown

(b) Stannous Chloride.

The curves for all the stannous chloride solutions measured are shown in figures I and II. It will be seen that with high chlorion concentration the curves tend to exhibit a maximum at about 218mμ (log k about 4.4), and that as the chlorion concentration decreases this maximum sinks and the absorption moves

* cf also (30)

towards shorter wavelengths until the curves approximate to the long - wavelength "half" of a simple band with a maximum below 200mμ . It is obvious that these curves cannot be due to the combined absorptions of Sn^{++} and Cl^- * but must represent the absorptions of quite other systems. The presence of unassociated Sn^{++} is most to be expected in solution 8 (8 I) a dilute (about 0.025 m) solution of $SnCl_2$ with the minimum amount of added HCl needed to suppress hydrolysis, but it can easily be shown in a semi-quantitative way that even in this solution other ions than Sn^{++} and Cl^- must be present. On the assumption that, say, half the tin in solution 2 is present as Sn^{++}, and that the portion of curve 2, VI between 200 and 205mμ represents the absorption due to this half, $k_{Sn} = 2k_{2VI}$, or $\log k_{Sn} = \log k_{2VI} + 0.301$. Hence, as the ratio $[Cl^-] : [Sn]^\dagger$ in solution 8 = 3.7, $k_{Sn} + 3.7k_{Cl^-}$ should equal k_{8I} if solution 8 contained only Sn^{++} and Cl^-. That this is not the case is seen by a comparison of the eighth and last columns in the following table, which shows the quantities under discussion for the wavelengths 200 and 205mμ. And as half is probably a low esti-

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* The absorption of Cl^- is shown in Fig. VI (taken from original measurements for 17).

† Here, and in what follows, [Sn] refers, of course, to the concentration of stannous tin as determined.

λ in $m\mu$	log k for 2,VI	log k_{2VI} + 0.30 = log $k_{Sn^{++}}$	$k_{Sn^{++}}$	log k_{Cl^-} (see below)*	log k_{Cl^-} - log (0.57)	3.7 k_{Cl^-}	k_{Sn} + 3.7 k_{Cl^-}	log k_{8I}	k_{8I}
200	3.40	3.70	5012	1.18	1.75	56	5068	4.31	20420
205	2.99	3.29	1950	0.27	0.84	7	1957	4.20	15850

* From original measurements for 17.

mate for the amount of tin present as Sn^{++} in solution 2, use of a higher figure would make the discrepancy as shown above even greater.

As the co-ordination number of the stannous ion is apparently four (6, vol. 7), we should expect to find no other complexes present than $SnCl^+$, $SnCl_2$, $SnCl_3^-$ and $SnCl_4^{--}$, and this is supported by PRYTZ'S results (27 and table I). We should also naturally expect that the higher the chlorion concentration for a given concentration of tin the greater should be the proportion of the more saturated complexes, and PRYTZ'S results again confirm this. The fact that the curves move towards longer wavelengths with increasing chlorion concentration (see, e.g., the series 8,5,6,4 of Fig.I) then shows that the absorptions for the more saturated complexes lie at longer wavelengths than those for the less saturated. Hence the absorption at the longer wavelengths will be mainly determined by the absorption and concentration of the most saturated complex present,

while towards the head of the curve the absorptions of the different complexes will be superimposed. It will in fact be noticed that the curves of all the solu - tions where $[Cl^-]$ is greater than 1.5 molar show a characteristic form in their lower part with two "waves" at about 260 - 265 mμ and 280 - 285 mμ, and that this form remains substantially unchanged over the range 7.6 - 1.5 of $[Cl^-]$, but that over the same range the upper (log k>4) parts of the curves alter considerably. It might be thought at first that the ruling factor in complex formation would be the value of the ratio $[Cl^-] : [Sn]$, a high value of this ratio favouring a high degree of binding of the chlorions in complexes, but a glance at the curves shows that this is not the case: <u>the main factor in determining the extent of complex formation is the chlorion concentration alone</u>. For the series of curves 7, 9, 10, 11, 12, 13 (II) we see that the degree of complex formation apparently decreases in the order

$$7 > 12 > 10 > 11 > 13 > 9$$

Now for these solutions, while $[Cl^-] : [Sn]$ decreases in the order

$$12 > 13 > 11 > 10 > 9 > 7$$

for $[Cl^-]$ the order is

$$7 > 12 > 10 > 11 > 9 > 13$$

i.e., the degree of complex formation follows closely the value of $[Cl^-]$, and not of $[Cl^-] : [Sn]$. Again,

while solutions 4 and 10 have $[Cl^-]$ values of the same order (5.03, 3.67 respectively), the ratios $[Cl^-]$: $[Sn]$ differ greatly (3.7, 248 respectively) and yet the two solutions show extremely similar absorption curves (4 I and 10 II).

It can be shown however that this dependence on $[Cl^-]$ is truly a consequence of the Law of Mass Action. For the equilibrium

$$SnCl_n^{(n-2)-} \rightleftharpoons SnCl_{n-1}^{(n-3)-} + Cl^-$$

we have

$$K = \frac{\left[SnCl_{n-1}^{(n-3)-}\right]\left[Cl^-\right]}{\left[SnCl_n^{(n-2)-}\right]} \quad \text{- - - - - - - - - - (4)}$$

i.e., the formation of more saturated from less saturated complexes is dependent to a first approximation only on the concentration - or, strictly speaking, the activity - of the chlorion. Hence arises the change in the curves (discussed above) when the solutions are diluted, changing $[Cl^-]$ but not the order of magnitude of $[Cl^-]$: $[Sn]$. (The impossibility of keeping a constant ratio $[Cl^-]$: $[Sn]$ on dilution has been explained above).

(3 I) is the absorption of a pure concentrated solution of $SnCl_2$ in water. This unfortunately could not be meausred above log k = 3.4, as for this a thinner layer of solution than that afforded by the smallest cell available (0.0001mm.) would be needed, at this concentration. However, enough of the curve is

given to show that it has a substantially similar form to that of other solutions with approximately equal chlorion concentration (= 2.63 x 2 = 5.26m). Complex formation could of course take place in this solution according to the equation

$$2SnCl_2 = SnCl_3^- + SnCl^+$$

$$3SnCl_2 = SnCl_4^{--} + 2SnCl^+ \qquad \text{etc.}$$

A process such as

$2\ SnCl_2 = SnCl_4^{--} + Sn^{++}$ is unlikely owing to the ease with which free Sn^{++} ions add on OH^- (hydrolysis). Undissociated $SnCl_2$ will doubtless also be present. Conductivity data for a concentrated solution of $SnCl_2$ would be interesting, but I was unable to find these in the literature.

Solutions 9 and 13 present an anomaly in that 9 (9 II) seems to exhibit a less degree of complex formation than 13 (13 II) although 9 has a greater chlorion concentration. The explanation is, perhaps, to be found in a specific influence of the added kation; since the Cl^- of 9 is added as HCl, but of 13 mostly as KCl, such an influence would mean a greater stability of complexes formed with KCl and $SnCl_2$ than of those with HCl and $SnCl_2$. YOUNG (23) also concluded that the KCl complexes were more stable.

It will be of interest to calculate the actual amounts of the different complexes present in these solutions according to the method given by PRYTZ

TABLE 3.

Sol. No.	7	8	9	10	11	13
Curve	7II	8 I	9 II	10 II	11 II	13 II
Conc. Stannous tin. (moles/litre)	0.0753	0.0259	0.00869	0.0148	0.00553	0.00214
Conc. HCl.	7.484	0.0447	1.497	------	0.520	0.340
Conc. KCl.	---	----	---	3.624	1.632	0.726
Total Conc. Cl^-	7.635	0.0965	1.527	3.674	2.163	1.074
%age of various complexes present.						
Sn^{++}	0.0_314	31.5	0.2	0.05	0.2	1.2
$SnCl^+$	0.0_213	51.7	4.0	2.6	6.3	15.6
$SnCl_2$	1.4	15.8	35.0	18.6	30.0	43.6
$SnCl_3^-$	6.4	0.9	32.4	41.1	39.5	28.5
$SnCl_4^{--}$	92.3	0.02	28.3	37.5	24.0	11.0
Total	100.1	99.9	99.9	99.85	100.0	99.9

(27). As the method is only applicable where the stannous salt concentration is small (PRYTZ used 0.01m), the calculation was done for solutions 7, 8, 9, 10, 11 and 13. The results are shown in table 3. In making the calculations, the activity coefficient for the stanno-ion was taken as a function of the ionic strength as in (27) and the values of the activity coefficients for the added halide were got by interpolation of the values for 25° given in LANDOLT-BORNSTEIN's "Physikalisch-Chemische Tabellen", supplementary vol. IIb. Where both KCl and HCl are present the value for the activity coefficient used was the statistical mean of the activity coefficients of HCl and KCl at the appropriate concentrations.

We see from table 3 that the extent of the complex formation as shown by these calculations runs parallel to that shown by the absorption curves, except in the case of solutions 9 and 13(discussed above). Comparing table 3 with the curves, we see that 7 II must represent very nearly the absorption of pure $SnCl_4^{--}$ and 8 I mainly $SnCl^+$. It would be interesting to obtain the individual absorption of each of the various complexes, and this is apparently feasible, by the following method. Taking, say solutions 7, 9, 10, we may consider only $SnCl_2$, $SnCl_3^-$ and $SnCl_4^{--}$ to be present. Now in an absorbing solution containing three components we have for the extinction at any

wavelength.

$$E = kcd = (k_1c_1 + k_2c_2 + k_3c_3)d \quad . \quad . \quad . \quad (5).$$

where k_1, k_2, k_3 are the absorption coefficients of the three components, and c_1, c_2, c_3 their concentrations, and k the measured absorption coefficient. Hence in the present case we will get at each wavelength from each curve an equation in k, k_1, c_1, k_2, c_2, k_3, and c_3. (Having put c = 1, c_1, etc., become 1/100 the percentages given in table 3), That is, from the three curves we get three equations in the three unknowns k_1, k_2, k_3. Hence these quantities, here the absorption coefficients of $SnCl_2$, $SnCl_3^-$, $SnCl_4^{--}$, are determinate, and by evaluating them for different wavelengths we may arrive at the absorption curves of the various complexes.*

There is, however, the serious objection that, if the absorption and concentration of solutions 9 and 13 have really been correctly measured, then PRYTZ's method of calculation cannot be applicable to solutions containing KCl in place of HCl. In that case, we cannot except the results quoted in table 4, for solutions 10, 11, and 13, and we cannot frame a series of equations from 7, 8, and 9 as 5 unknowns would be involved. In spite of these objections, however, I thought it worth while to make the calcula-

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* The absorption of the chlorion may be neglected at wavelengths above 205m (17).

tions, as outlined above for $SnCl_4^{--}$, $SnCl_3^-$, and $SnCl_2$, using the compositions given in table 4 for (1) 7, 9, 10 and (2) 7, 10, 13. (The absorption curve of solution 11 is, unfortunately, too uncertain below λ 225mμ). The results varied considerably, according to which set of curves was used, and also according to the exact way in which the unknowns were derived from the three equations, but they were sufficiently concordant to show that:

1- The absorption of $SnCl_4^{--}$ coincides very nearly with curve 7 II (for which $\lambda_{max.}$ = 218.5mμ and log $k_{max.}$ = 4.443) both in height (value of log $k_{max.}$) and position (value of $\lambda_{max.}$).

2- The absorption of $SnCl_3^-$ lies a little farther into the ultra-violet, and the band is somewhat higher ($\lambda_{max.}$ = 213 - 216mμ; log $k_{max.}$ = 4.5 - 4.8).

3- The absorption of $SnCl_2$ lies considerably farther in the ultra-violet: (no maximum at λ greater than 205mμ; log k at 210mμ = 4.14 - 4.2).

Another method of finding the individual absorptions was also tried: namely, to start from the assumption that curve 7 II represented the absorption of $SnCl_4^{--}$ only. Subtraction of this from 10 II (neglecting the $SnCl_2$ absorption) gave a provisional absorption curve for $SnCl_3^-$, and these two were then used in conjunction with one of the other curves of Fig. II, to get the absorption of $SnCl_2$. With these

provisional values a more accurate curve for $SnCl_4^{--}$ was obtained from 7 II, with this and the provisional $SnCl_2$ curve we obtain the $SnCl_3^-$ curve from 10 II, and a second more accurate curve for $SnCl_2$ was then got. With this, a final recalculation of the $SnCl_3^-$ absorption from 10 II was made. The results of this again lay within the limits of the results of the first method.

(c) K_2SnCl_6.

The absorption of this stannic compound was measured in order to see if the possible presence of the products of atmospheric oxidation would greatly affect the measured absorptions, calculated on the basis of the stannous tin content. 14 VI shows the absorption of a concentrated aqueous solution of K_2SnCl_6,* and we might expect it to represent the absorption of either undissociated K_2SnCl_6, or of the ion $SnCl_6^{--}$. On dilution, and addition of a large excess of Cl^- (solution 15), the absorption changes to that shown in curve 15 VI. In solution 15, the ratio $[HCl] : [K_2SnCl_6] = 3.54 : 0.00490 = 722$, and curve 14a VI shows $\log (k_{14\,VI} + 722k_{Cl^-})$. Hence, since 15 VI is widely divergent from this, there is probably a greater degree of complex formation in solution 15 than in 14; i.e., the complex ion $SnCl_6^{--}$ seems to be dissociated

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* I am indebted to Herr E. Doehlemann for the measurement with a vacuum spectrograph of that portion of this curve at λ 190 - 205mμ.

even in 0.6 molar solution. 16 VI shows the absorption of solution 15 diluted 1:10; the complexes have apparently to a large extent broken up. In fact, the behaviour of the stannic compound seems to run parallel to that of the stannous.

However, we see that the effect of the presence of stannic tin in the stannous chloride solutions measured will be very slight. Taking curves 7 II and 15 VI, let us calculate the error at the maximum of 7 II (log k = 4.443, λ = 218.5mμ) caused by the presence of various amounts of the absorbing substance of solution 15 over and above the stannous tin concentrations of solution 7. The corrected absorption for 7 II is given by

$$k = k_{7II} - ck_{15VI} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where c is the concentration (referred to the stannous tin concentration of 7 as unity) of stannic salt in 7, and k the true absorption of the stannous complex in 7. Working this out for a range of values of c 0.02 to 0.4 (i.e., 2% - 40% stannic tin in 7) we get:

$\log k_{7II}$ at 218.5mμ = 4.443

% stannic tin:	0	2	5	10	20	40
log k (corrected)	4.443	4.441	4.438	4.432	4.422	4.399
error:	0	.002	.005	.011	.021	.044

Thus itis seenthat 5% of the stannic salt would produce an almost negligible error in the absorption, and that even with as much as 20%, the error would be quite small.

(d) Stannous Bromide:-

The absorption curves of all the stannous bromide solutions measured are shown in figures III and IV. They are in general characteristics similar to the stannous chloride curves, tending to a maximum at about 245mμ(log k = about 4.5) with high bromion concentration, while the maximum disappears and the absorption moves towards shorter wavelengths on dilution. As with the stannous chloride curves, the absorption is obviously not due to the added absorptions of Sn^{++} and Br^{-}. (In figure III the absorption of the bromion is added for comparison; taken from the original measurements for (17). Four of the curves show definite maxima ; these are shown in table 4:-

TABLE 4.

Fig. III	curve 17;	max^m at 234mμ;	log k =	4.107
Fig. IV	do. 23	do. do 245mμ;	do.	4.443
Fig. IV	do. 26	do do 243.5mμ	do	4.451
Fig. IV	do 29	do do 243.5mμ	do	4.459

Those parts of the curves rising steeply above log k = 4.5 represent of course merely the absorption of Br^{-}; as log k for the curves was calculated on the tin concentration, the curves will show the Br^{-} absorption raised vertically by log $\left([Br^{-}]/[Sn]\right)$.

As we should expect from what has been said above, the curves indicate that for small tin concen-

trations the degree of complex formation depends on the bromion concentration and not on the ratio $[Br^-]/[Sn]$. Thus we see that curves 26 and 29 IV are almost identical; while solutions 26 and 29 have nearly equal bromion concentrations (3.9 and 4.2 respectively), the ratio $[Br^-]/[Sn]$ are very different (45 and 243 respectively). Again for solutions 17, 18, 19, 20 (curves 17 - 20 III) $[Br^-]$ increases in the order $20 < 19 < 18 < 17$.
while $[Br^-]/[Sn]$ increases in the order
$17 < 18 < 19 < 20$.
A glance at figure III shows that complex formation apparently increases exactly in the same order as the bromion concentration.

A comparison, however, of the curves for 26 and 17 shows that with high tin concentrations the extent of complex formation cannot be dependent solely on the bromion concentration. While these two solutions have very similar bromion concentrations, $[Sn]$ in solution 17 is as high as molar. We can see from equation (4) that where the tin and halide ion concentrations are of the same order of magnitude the extent of the complex formation can no longer, even to a first approximation, be dependent on the halogen - ion concentration only, thus confirming what is shown by curves 17 III and 26 IV.

A priori, we should expect in these solutions

any or all of Sn^{++}, $SnBr^{+}$, $SnBr_2$, $SnBr_3^{-}$ and $SnBr_4^{--}$ to be present. PRYTZ, however, in measurements on solutions containing up to twice molar bromion, found no indications of complexes higher than $SnBr_3^{-}$, (27). In table 5 are shown the compositions, calculated according to PRYTZ's method of solutions 19, 24, 25 and 26.

TABLE 5

Solution No	19	24	25	26
Curve	19 III	24 IV	25 IV	26 IV
Concentration Stannous tin (moles/litre)	0.080	0.0141	0.00322	0.0878
Concentration HBr	0.328	1.349	0.270	0.099
Concentration KBr	-----	-----	-----	3.636
Total concentration Br^{-}	0.488	1.377	0.276	3.933
%age of various complexes present.				
Sn	11.1	1.2	24.8	0.2
SnBr	31.5	8.8	38.4	4.5
$SnBr_2$	47.3	55.7	32.7	34.7
$SnBr_3^{-}$	10.3	34.2	4.0	60.8
Total	100.2	99.9	99.9	100.2

But as we have no evidence that solutions stronger in bromion than 2 - molar may not contain some $SnBr_4^{--}$, the distribution of the tin among the complexes given for solution 26 must be accepted with reserve. Accepting, however, these figures for the moment we

see that 19 III and 25 IV must represent approximately the absorption of ($SnBr^+ + SnBr_2$), 24 IV of ($SnBr_2 + \frac{1}{2} SnBr_3^-$ and 26 IV of ($SnBr_3^- + \frac{1}{2} SnBr_2$). This is perfectly in accord with the form of the curves if we assume that, in an analogous fashion to the stannous chloride complexes, $SnBr_3^-$ has an absorption band with a maximum at about 244mμ, while the maximum of absorption of $SnBr_2$ and SnBr lie below 225mμ. Also, if 61% is a true figure for the amount of $SnBr_3^-$ in 26, and if there is really no $SnBr_4^{--}$ present, then, assuming that the absorption of $SnBr_2$ and $SnBr^+$ is comparatively very small at 244mμ (which is justified by curve 25 IV, solution 25 containing 4% $SnBr_3^-$ only), the maximum of the $SnBr_3^-$ band must lie at a height given by

$$\log k_{max.}(SnBr_3^-) = \log k_{max.}(26) + \log \frac{100}{61} \quad \ldots(7).$$
$$= 4.45 + 0.22$$
$$= 4.7 \text{ approximately.}$$

This figure falls within the limits suggested (p.52) for $\log k_{max.}(SnCl_3^-)$.

While solutions 26 and 29, containing 3.9 and 4.2 molar bromion respectively, have practically identical absorption at λ 230mμ, we see that the absorption of solution 23 (23 IV), where $[Br^-] = 6.5m$, shows a displacement towards longer wavelengths. The maximum of absorption is displaced (table 4) by 1.5mμ, while most of the rest of the curve is displaced by

at least 3mμ. This seems to be evidence for the formation at this high bromion concentration of considerable amounts of $SnBr_4^{--}$. The maximum of absorption for this complex apparently lies in the neighbourhood of 250mμ.

Curves 19 - 22 III represent the progressive dilution of a solution of $SnBr_2$, with the addition in each case, if necessary, of as little HBr as was necessary to prevent visible hydrolysis. In solution 19, we have still a considerable extent of complex formation (table 5), and we see how on each dilution 1:10 the upper part of the curve tends more and more to approximate simply to the absorption of Br^- raised by an amount $\log\left([Br^-]/[Sn]\right)$. This is shown by the following table.

λ =	205	210	215	220mμ
$\log k_{21}$	5.030	4.680	4.180	3.809
$\log k_{22}$			4.155	3.658
$\log k_{Br^-}$	3.680	3.300	2.730	2.095
$\log k_{Br^-}$ +log 21.8	5.019	4.639	4.069	3.434

The abnormal flatness of the lower portion of these curves (and also of 28 IV) is an indication of hydrolysis of the solution. Under these circumstances the true absorption becomes masked by the dispersion caused by the products of hydrolysis. As the solutions remained clear to the eye, these products

must have been present in a colloidal disperse state. This effect is discussed in section VIf below. A comparison of curves 21 and 21a III is also interesting. 21 III was taken immediately, and 21a III after an interval of 5 days. We see how in that time the amount of complex-bound tin (absorption at 225mμ) has decreased, and the extent of the dispersion (flatness of lower portion of the curve) increased. This may indicate oxidation, which could of course take place very easily at this high dilution, but as the flask was filled with CO_2 and carefully sealed up, it seems more likely that it indicates hydrolysis proceeding quite slowly.

(e) Stannous Iodide

The curves for the stannous iodide solutions are shown in figure V. The general characteristics are again the same, indicating complex formation by the appearance of a maximum at about 290mμ when the iodion concentration is high. But these solutions behave differently from the $SnCl_2$ and $SnBr_2$ solutions, as on decreasing $[I^-]$ there is not so much a displacement of the absorption towards shorter wavelengths, but rather a vertical displacement (sinking) of the maximum. Thus, for solutions 36, 31, 32, 33, we have:-

Solution No.	36	31	32	33
$[I^-]$ . . .	6.073	2.785	1.320	0.754
Pos'n of maximum) or point of inflection)	288.5mμ	289	286.5	(290)
log k at do. do.	4.730	4.440	4.200	3.668

(These figures are rather uncertain, especially the last, on account of the flatness of the curves and the irregularity of the points). As before, the steeply-rising portions at the short wavelength end represent the iodion absorption raised by an amount $\log\left([I^-]/[Sn]\right)$.

The behaviour of these curves is best explained by assuming that we are dealing here with one definite complex - say SnI_3^- - which breaks up on dilution not into simpler complexes but directly into its component ions - Sn^{++} and I^-, On that assumption it would be interesting to calculate the degree of dissociation of the complex (or, conversely, association of stannous iodide) at each iodion concentration. For this we must first of all assume that in solution 36 all the tin is present as the complex. This is justified by the high iodion concentration and the high value (4.729) of log k of the maximum. Hence, if we then subtract from the absorption of solution 36 the absorption due to the excess of the iodion present we should get the absorption of the pure complex. Whether that complex is SnI_3^- or SnI_4^{--} is here immaterial. For, if $[Sn]$ and $[I^-]$ are the analytically determined concentrations of stannous tin and iodion respectively, we have, if the complex is SnI_3^-:

$$k_{36} = k_{SnI_3^-} + k_{I^-} \cdot \frac{[I] - 3[Sn]}{[Sn]}$$

and if it is SnI_4^{--}:

$$k_{36} = k_{SnI_4^{--}} + k_{I^-} \cdot \frac{[I^-] - [4\ Sn]}{[Sn]}$$

But as $[Sn]$ is very small compared with $[I^-]$, we may replace both $([I^-] - 3[Sn])$ and $([I^-] - 4[Sn])$ by $[I^-]$, and hence we get:

$$k_c = k_{36} - \frac{[I^-]}{[Sn]} \cdot k_{I^-} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k_c is the absorption coefficient of the complex.

Curve 36a V shows the absorption of the complex as determined by this means.

An analysis of curves 31, 32, and 33 (V) by equation (8) gives the absorptions due to the amount of complex present in each case. These are shown as curves 31a, 32a, 33a (V). The degree of dissociation is now calculated as follows.

Let k_m be the measured absorption coefficient.

Let k_I be the absorption coefficient of I^-.

Let k_x be the absorption coefficient of the complex.

Let α, β be the degree of dissociation of the complex, and of association of SnI_2, respectively, at each iodion concentration ($\alpha + \beta = 1$).

Let c_I be the concentration of I^-

Let c be $[Sn]$, taken here as the concentration of dissolved SnI_2.

Then concentration of complex = $c\beta$

Hence, assuming (1) that the complex is SnI_3^- and (2)

that the Sn not present as complex has no absorption in the region $\lambda > 275 m\mu$ we have

$$k_m c = k_I (c_1 - c\beta) + k_x c\beta \quad \ldots\ldots\ldots (9)$$

Therefore:

$$k_m = k_I (c_1/c - \beta) + k_x \beta \quad \ldots\ldots\ldots (9a)$$

But β may be neglected in comparison with c_1/c_2. Therefore

$$k_m = k_I c_1/c + k_x \beta \quad \ldots\ldots\ldots (10)$$

(If the complex were SnI_4^{--} we would have 2β in place of β within the bracket in equation (9a) but this could likewise be neglected, giving the same form for equation (10).

Hence $$\beta = \frac{k_m - k_I \cdot c_1/c}{k_x} \quad \ldots\ldots\ldots (11)$$

Curve 36a V gives k_x, and the other analysed curves 31a - 32a V give $k_m - k_I c_1/c$ in each case. Therefore, taking logs, the difference between the ordinate of any analysed curve and the ordinate at the same wavelength for 36a V must give $- \log\beta$. Theoretically, if only SnI_3^- is present in each case, all the analysed curves should have the same form, but as the very flat form of the measured curves in the region 270 - 300mμ makes accurate measurement extremely difficult, the approximation of the various analysed curves to the form of 36a V may be taken as reasonably good. Using the difference in the ordinates at the maxima (288.5mμ), the values of β were calculated; they are shown in table 6. (In the case of 32a V the maximum shows a

slight displacement, and the value of log k at 283mμ was used). The values of β found are graphed against $[I^-]$ in figure 4.

TABLE 6.

Solution No.	log $k_{max.}$ of analysed curve	Δlog $k_{max.}$ (= - logβ)	(β= degree of association)	$[I^-]$
36	4.700	0	1	6.073
31	4.439	0.261	0.55	2.785
32	4.174	0.526	0.30	1.320
33	3.620	1.080	0.083	0.754

It is impossible to say definitely whether the complex is SnI_3^- or SnI_4^{--} but it is highly probable that it is SnI_3^-, for the following reasons:

1- Since the complex $SnBr_4^{--}$ is less easily formed than $SnCl_4^{--}$ we should expect SnI_4^{--} to be still less easily formed (at comparable halogen-ion concentration).

2- Assuming that the stannous iodide is really all present as complex in solution 36, this gives a value of log $k_{max.}$ of 4.7 for the complex and this differs from the corresponding value for $SnCl_4^{--}$ but lies within the limits of the value for $SnCl_3^-$. It is also in agreement with YOUNG's conclusions (22) that the complex formed should have the formula SnI_3.

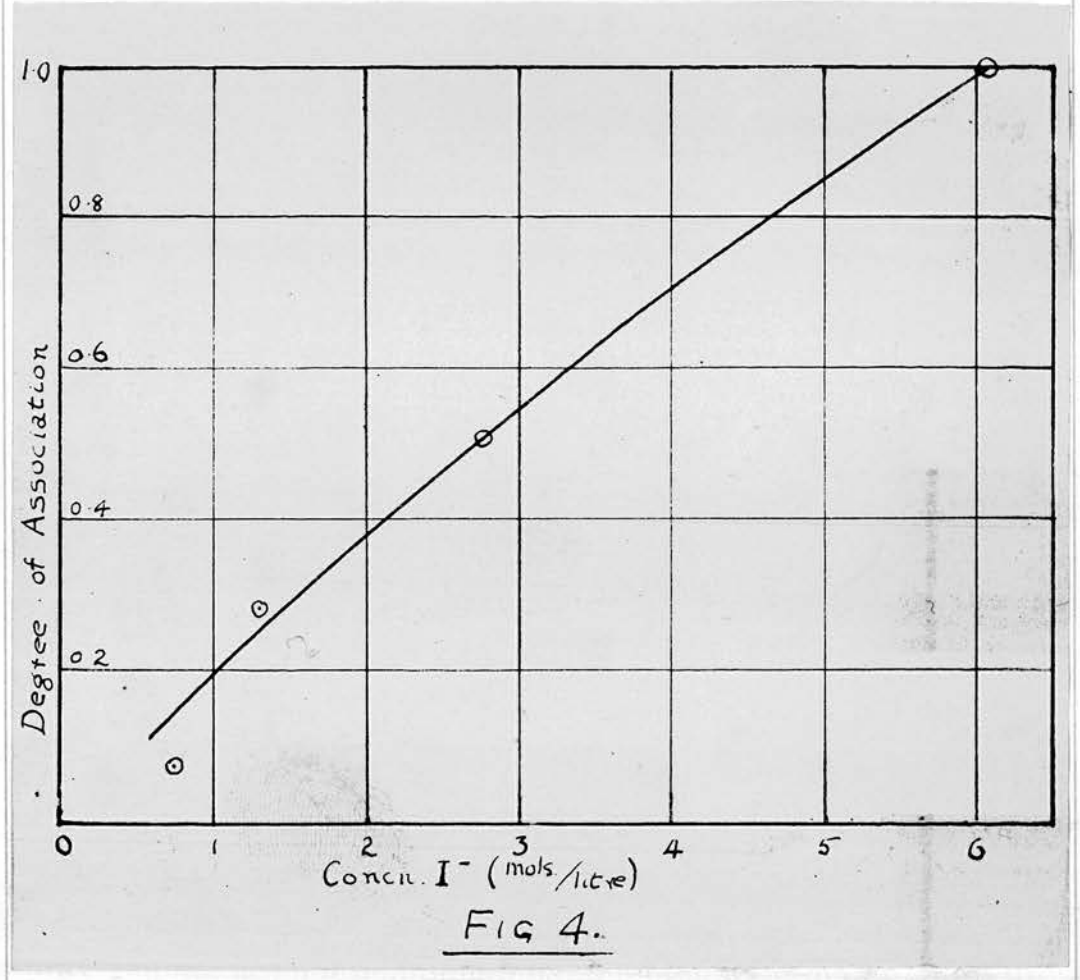
1·0
0·8
0·6
0·4
0 2
Degree of Association
0
1
2
3
4
5
6
Concn. I⁻ (mols/litre)

FIG 4.

(f) Hydrolysis of the Solutions.

It was mentioned in the discussion of the stannous bromide curves that the abnormal flatness of the lower part of certain of them indicated hydrolysis of the solutions. This effect is still more clearly seen in the case of the more dilute SnI_2 solutions (34 and 35 V). As in the case of the stannous bromide solutions, this flat portion of the curves must represent dispersion by the colloidal products of hydrolysis.

If we are measuring the amount of light transmitted, then dispersion is, of course, indistinguishable from absorption. RAYLEIGH's formula (55) for the loss of light by dispersion may be written (FROMHERZ) as:-

$$-\frac{dI}{d_x} = \frac{Nv^2}{\lambda^4} \cdot \frac{24\pi^3}{1000} \cdot I \left(\frac{\left(\frac{n_1}{n}\right)^2 - 1}{\left(\frac{n_1}{n}\right)^2 + 2} \right)^2 \quad . \quad . \quad (12)$$

where I is the intensity of light,

x is path of beam,

N is number of particles per litre,

v^2 is mean square volume of particles in c.c.,

λ is wavelength of the light

n, n_1 are refractive indices of dispersion medium and of particles, respectively;

and the particles are assumed to be infinitely small in comparison with λ. Hence we see that for a given dispersing medium and light intensity, and assuming that n_1/n does not vary with the wavelength,

$$-\frac{dI}{d_x} \propto \frac{I}{\lambda^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we now, as we may, rewrite the BEER-LAMBERT law in the form:

$$-\frac{dI}{d_x} = I \cdot c \cdot \frac{k}{0.4343} \quad . \quad . \quad . \quad . \quad (14).$$

and compare (13) and (14), we see that for k, which is the absorption coefficient that we measure,

$$k \propto 1/\lambda^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where the "absorption" is due to dispersion.

Taking logs, we get

$$\log k = -4 \log + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where C is a constant.

In figure V is shown the curve (curve 37) for equation (16), 4 log λ being plotted against λ, and an arbitrary value of the constant C being chosen to bring the curve to a convenient height. It will be seen that the lower portions of 34 and 35 V* resemble this theoretical curve very closely. The agreement is really remarkable, considering the following points:

1- The particles may be of appreciable size compared with λ;

2- n_1/n may not be independent of λ;

3- it is extremely difficult to choose the points of equal blackening on the plates when the absorption curve is so flat.

(g) Comparison of the results for Stannous Chloride Bromide and Iodide:-

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* We can really consider 34 V only as 35 V has too few measured points for its true shape to be known with any degree of certainty.

If we compare the sets of curves for the three halides (Cl, figures I, II; Br, figures III, IV; I, figure V) we see that as we pass in the order Cl - Br - I the shift towards shorter wavelengths of the absorption as a whole becomes replaced by a sinking parallel to the lgg k axis of the maximum which develops at large halide concentrations. As the available evidence shows that the tendency to form saturated complexes decreases in the same order (Cl > Br > I), we can most easily interpret this fact by supposing that the separation between the bands for the various individual complexes increases as we pass from Cl to I. This falls into line with the increasing separation in the order Cl < Br < I shown by the two maxima of absorption of the halide ions, (19 p. 372).

As we pass from Cl to I the separation of the complex band from the simple halide ion band also increases:-

$\lambda_{max.}$	Hal^-	Cl		Br		I
		181		190	195	194	226
$\lambda_{max.}$	$SnHal_n$	218		243		290	
$\Delta\lambda$		37		53	48	96	64

The frequency difference between the complex maximum and the longer wavelength maximum of the halide ion remains approximately constant, but that between the complex maximum and the other halide ion maximum increases from 9300 cm^{-1} for Cl to 17000 cm^{-1} for I. As the

absorption of these complexes is probably due to the halide ion only (see 19, p. 373, also section VIIc below), this is only to be expected when we remember that the polarisability increases in the order Cl < Br < I (9), and hence the natural frequency of the halogen atom will on being bound in a complex show an increasing alteration in the same order.

In this connection it is interesting that one maximum of absorption for the ion I_3^- (56. Also figure VII here) coincides with the maximum of absorption ascribed to SnI_3^- (36a V); $\lambda_{max.}$ = 288 - 290 for both. (But see also section VIIc below).

VII. MEASUREMENTS IN ALCOHOLIC SOLUTION.

(a) Introduction

As an extension to the above work it was thought that measurements of the absorptions of the stannous halides in alcoholic solution might yield some interesting results. The measurement of stannous iodide in particular would also be a useful extension to the work of SCHEIBE (14) on other di-iodides. In view of his theory that the absorption is determined by the halogen atoms, the absorption of a stannic iodide solution was also measured. (The colours of stannous and stannic iodides are, of course, very nearly the same). For the sake of comparison, along with the curves for these solutions are shown also the absorption curves for iodine in two different solvents, alcohol and KI solution. (The absorption of iodine in KI - i.e., of the ion I_3^-, has also been measured by WINTHER, 56).

The effect was also tried of using water-alcohol mixtures instead of pure alcohol for the solutions of SnI_2 and SnI_4.

(b) Preparation of Solutions

$SnCl_2$, $SnBr_2$, and SnI_2 were as described above.

SnI_4:- This was prepared by the method of McDERMOTT (57). 12 grammes tin ("British Chemical Standards"

99.98% pure granulated) and 50 grammes A.R. iodine were refluxed in 75 grammes carbon tetrachloride (free chlorine, HCl and sulphur) until the violet colour of iodine vapour was gone. The SnI_4 was filtered off when cool, and twice recrystallised from carbon tetrachloride. Melting point 142.5° (uncorrected).

Ethyl Alcohol:- A very large number of different methods for purifying this substance have been given. As it was desired here to obtain a product with the greatest transparency in the ultra-violet, the method of CASTILLE and HENRI (58) which was specially designed to give a product suitable in this respect, seemed to be the most promising. After some experiment the following modification of the above method was adopted. Ordinary absolute alcohol was refluxed for 3-4 hours with 2 Gms. iodine per litre. 30-35 Gms metallic calcium per litre (to remove the iodine and water simultaneously) were then added, and the refluxing continued for a day. The alcohol was then distilled off, while a current of air dried by passage through a 5 foot tube filled with $CaCl_2$ was passed through it in order to remove any traces of ammonia. The first portion was rejected, in case it contained ammonia, and the distillation was stopped when about two-thirds had come over. The alcohol so obtained showed the following transmission:

In a 4 cm. layer to 230mμ.

In a 1 mm. layer to 215mμ.

(Exposure: just sufficient to record to about 208mμ in air). The spectrum down to the limit of transmission of the apparatus could easily be photographed through the alcohol using increased exposures.

The solutions were prepared by dissolving a weighed amount of the halide in alcohol, with subsequent dilution if necessary. For stannous chloride, the $SnCl_2 \cdot 2H_2O$ as used for the aqueous solutions was simply used without dehydration, as the amount of water thereby introduced (0.002 - 0.004% at the concentrations used) can hardly have been sufficient to produce any measurable effect. As the halides would probably not be ionised in alcohol, no special precautions were taken to avoid contact of the solutions with air, though they were not exposed to it any more than was absolutely necessary. The concentrations used in calculating log k were simply based on the weight of salt dissolved and, in the case of the stannous salts, the percentage of stannous tin in the dry salt; (this was in each case found by analysis to be slightly lower than the theoretical figure).

The solutions measured are shown in table 7, and all their absorption curves in Figure VII.

(c) Discussion of Results.

The curves for $SnCl_2$ and $SnBr_2$ present no

features of particular interest. It is evident, from a comparison of curves 1 and 2, and 3 and 4 VII with the supposed Sn (1 and 2 VI), the Cl^- (figure VI) and the Br^- (figure III) curves that the absorptions of the alcoholic solutions especially in the case of the $SnBr_2$ can hardly be due to any of these ions, "even allowing for a considerable displacement of the absorption in alcoholic solution". Hence curves 1, 2, 3, 4 VII probably represent the absorptions of undissociated $SnCl_2$ and $SnBr_2$, in alcohol; any sort of auto-complex formation at this small concentration is extremely unlikely. In figure 5 is shown the absorption of solution 3 compared with that of another dibromide in alcohol - $CdBr_2$, measured by SCHEIBE*(14).

The curves for the iodides show entirely different characteristics. Here two distinct bands, and indications of a third in the far ultra-violet are visible. It is seen that the absorptions of SnI_2 and SnI_4 (5, 6, 7, 9 VII) are identical in so far as the position of the bands is concerned. The absolute and relative height of the two bands is different but then these do not remain constant for one substance; notice for example, the effect of a com-

---

*Cd and Sn fall, of course, into the same period.

TABLE 7.

No. of Soln.	Solute	Solvent	Concentration in mols/litre
1	$SnCl_2$	EtOH	0.00128
2	$SnCl_2$	EtOH	0.00064
3	$SnBr_2$	EtOH	0.00124
4	$SnBr_2$	EtOH	0.000496
5	SnI_2	EtOH	0.000602
6	SnI_2	EtOH	0.000339
7	SnI_2	EtOH	0.0000668
8	SnI_2	EtOH with 10% water	0.000301
9	SnI_4	EtOH	0.000307
10	SnI_4	EtOH with 25% water	0.000307
11	SnI_4	EtOH with 50% water	0.000307
12	SnI_4	EtOH with 75% water	0.000307
13	I_2	EtOH	0.000804 (for $\underline{I_2}$)
14	I_2	0.0213m aqueous KI solution	0.000201 (for $\underline{I_2}$)

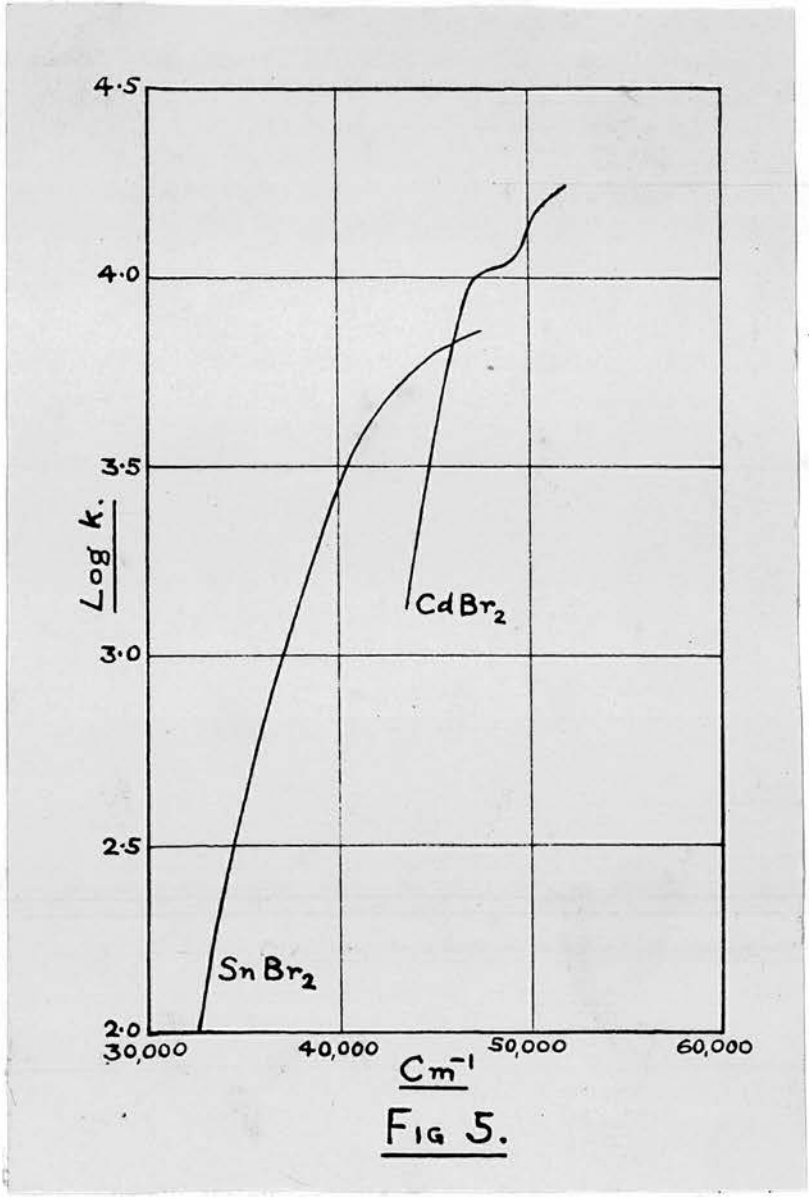

FIG 5.

paratively small variation in concentration on the relative heights of the two bands of SnI_2 (5, 6, 7, VII). An alteration of the state of the solvent produced by adding water to the alcohol is also seen to affect the absolute and relative heights of the bands considerably (8, 10, 11, 12 VII). In figure VII are also included the absorption of two iodine solutions (13 and 14 VII). These show again the same two bands; but in the case of the shorter wavelength band the maximum shows a small displacement (2 - 3mμ) towards shorter wavelengths. As mentioned above, the position of this maximum coincides exactly with that of the band ascribed to SnI_3^- (36a V). The exact position of the other band for iodine seems to depend on the solvent.

In figure 6 are shown the curves for solution 5, with the wavelengths re-calculated as wave numbers, and also SCHEIBE's (14) curves for the absorptions of ZnI_2, CdI_2, and HgI_2 in alcohol.

The absorption of SnI_2 is seen to be similar except that it shows three bands instead of two. SCHEIBE explains the two bands shown by the other iodides by assuming photochemical decomposition, yielding either a stable or a metastable iodine atom, and points out that the "Bandenanstiege" have a constant separation of 7000 - 8000 cm^{-1}, while the theoretical energy difference between the stable and metastable iodine atoms corresponds to 7600 cm^{-1}. The separation of the

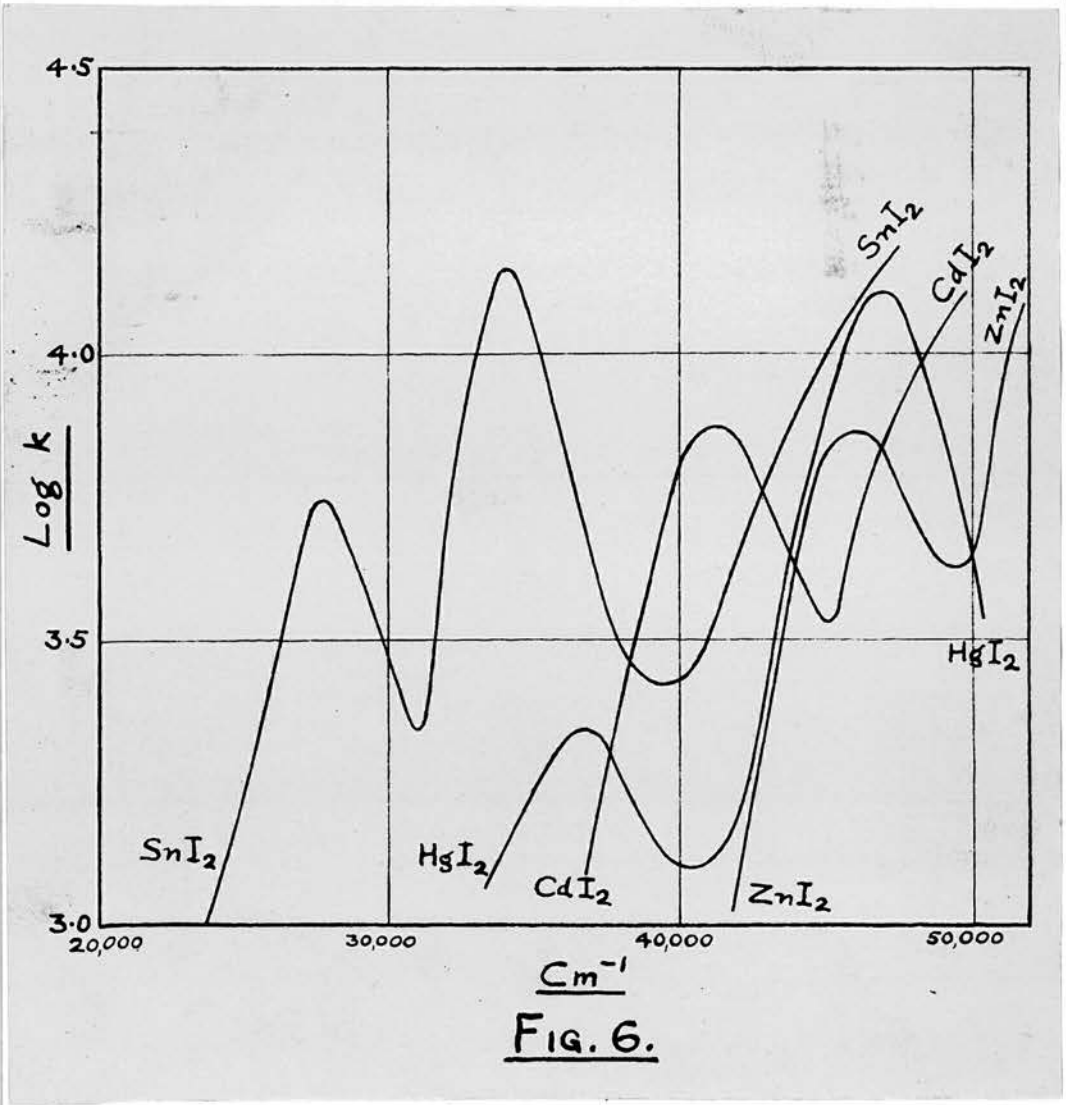
4·5
4·0
3·5
3·0
Log k
20,000
30,000
40,000
50,000
Cm⁻¹
SnI₂
HgI₂
CdI₂
ZnI₂
SnI₂
CdI₂
ZnI₂
HgI₂

FIG. 6.

two longer wavelength bands of SnI_2 is rather less than this, about 6000 cm^{-1}; while, taking the feet of the middle band and of the one lying farthest in the ultra-violet, their separation is about 8000 cm^{-1}. According to SCHEIBE, the two different states in which the iodine atom is split off are connected with the existence of two different forms of the iodine - a homopolar and a heteropolar. He further suggests that the relative heights of the two bands for Zn, Cd, and Hg iodides is a measure of the equilibrium between these two forms. It might be possible to apply a similar explanation to the absorption of the tin iodides, since the three curves for SnI_2 (5, 6, 7 VII) seem all to pass through a common point at 308mμ(log k = 3.82), and the existence of such a feature in a series of absorption curves is evidence that the absorbing substance presents an equilibrium mixture of two and only two forms,(59). However, the deduction that there is an equilibrium between two forms in SnI_2 can only be accepted with reserve, in view of the existence of the third band (far ultra-violet). Iodine present in homopolar union will be split off as an excited atom, and that in heteropolar union as a normal atom. Or the iodine might be split off in three states: i.e., if the first (long - wavelength) band is taken as representing the liberation of a neutral unexcited iodine atom, the next band the production of a metastable

(excited) iodine atom, then the third band might correspond to the energy necessary to raise the iodine atom to the next higher state of excitation. Alternatively, it might correspond to the splitting off of a second iodine atom. In the gaseous alkaline iodides there are similar indications of a band in the far ultra-violet, and FRANCK (60) explains this as representing the raising of the alkali atom to a higher state of excitation, but an analagous explanation seems to be out of the question here, on account of the same third band being shown by iodine (13 VII) as by SnI_2 and SnI_4. However, experimental data do not warrant further speculation on this point at present.

The fact that the absorptions of SnI_2, SnI_4 and iodine are so nearly identical certainly lends strong support to SCHEIBE's view that absorptions of this type are determined only by the halogen atoms present. While the 358mμ band is lower for SnI_4 than for SnI_2, the 290mμ band is for comparable concentrations. some two times higher ($\Delta \log k$ = about 0.3). This may be due to SnI_4 having twice the number of absorbing centres (I atoms), but in view of the pronounced dependence of the height of these bands on extra-molecular conditions the number two is probably a pure coincidence, and the difference must then be ascribed merely to the two compounds containing different proportions of molecules with iodine in homo- and heteropolar combination.

The dependence of the height of the bands on the nature (polarity) of the solvent is well illustrated by curves 8, 10, 11, 12 VII. The replacing of part of the solvent alcohol by water lowers both the 357mμ and 290mμ bands for SnI_2, while for SnI_4 it raises them and also reduces the difference in height between the two bands. The variation with concentration in the relative height of these two bands for SnI_2 in pure alcohol is, of course, on SCHEIBE's theory due to the dependence on concentration of the equilibrium between the different sorts of molecules.

VIII. SUMMARY AND CONCLUSIONS.

1. The absorption spectra of the following solutions have been measured: $Sn(ClO_4)_2$ in $HClO_4$; $SnCl_2$ in water, in HCl and in KCl; $SnBr_2$ in HBr and in KBr; SnI_2 in KI; K_2SnCl_6 in water and in HCl; $SnCl_2$ in alcohol; $SnBr_2$ in alcohol; SnI_2 in alcohol and in alcohol and water; SnI_4 in alcohol and in alcohol and water; I_2 in alcohol and in KI solution.

2. The absorptions of all the aqueous solutions of the stannous halides indicate a considerable degree of complex formation, which was dependent chiefly on the halide concentration.

3. The results for $SnCl_2$ and $SnBr_2$, were discussed in the light of the previous results of PRYTZ on complex formation by these salts. A tentative attempt was made to elucidate the individual absorptions of the different Sn - Cl and Sn - Br complexes.

4. It was found possible to estimate from the results for SnI_2 in KI the variation of the degree of association of SnI_2 with the total iodine concentration.

5. Stannous and stannic iodides and iodine, were all found to have a similar absorption in alcohol; and the absorption of the tin iodides were discussed in the light of a hypothesis put forward by SCHEIBE to explain the absorption shown by other iodides in alcoholic solution.

In conclusion, I wish to thank Dr. Hans

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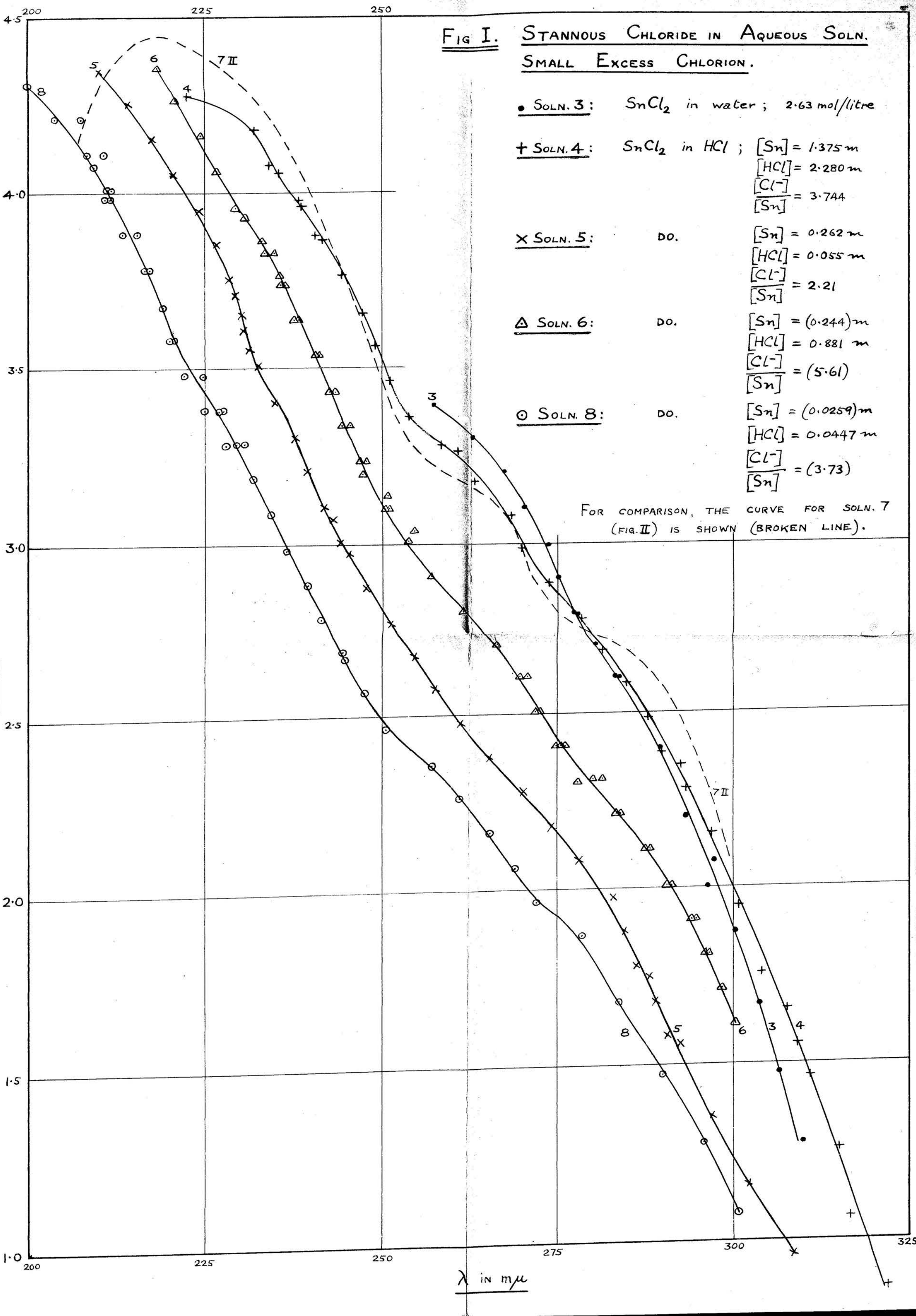


FIG I. STANNOUS CHLORIDE IN AQUEOUS SOLN. SMALL EXCESS CHLORION.

• SOLN. 3: $SnCl_2$ in water; 2·63 mol/litre

+ SOLN. 4: $SnCl_2$ in HCl; $[Sn] = 1.375\ m$, $[HCl] = 2.280\ m$, $\frac{[Cl^-]}{[Sn]} = 3.744$

× SOLN. 5: DO. $[Sn] = 0.262\ m$, $[HCl] = 0.055\ m$, $\frac{[Cl^-]}{[Sn]} = 2.21$

△ SOLN. 6: DO. $[Sn] = (0.244)\ m$, $[HCl] = 0.881\ m$, $\frac{[Cl^-]}{[Sn]} = (5.61)$

⊙ SOLN. 8: DO. $[Sn] = (0.0259)\ m$, $[HCl] = 0.0447\ m$, $\frac{[Cl^-]}{[Sn]} = (3.73)$

FOR COMPARISON, THE CURVE FOR SOLN. 7 (FIG. II) IS SHOWN (BROKEN LINE).

FIG. II. STANNOUS CHLORIDE IN AQUEOUS SOLN.

LARGE EXCESS CHLORION.

⊙ SOLN. 7; $SnCl_2$ in HCl; $[Sn] = 0.0753$ mol/litre $[HCl] = 7.484$ m
$[Cl^-]/[Sn] = 101.3$

⊡ SOLN. 9: do. $[Sn] = 0.00869$ m, $[HCl] = 1.497$ m, $\frac{[Cl]}{[Sn]} = 175.9$

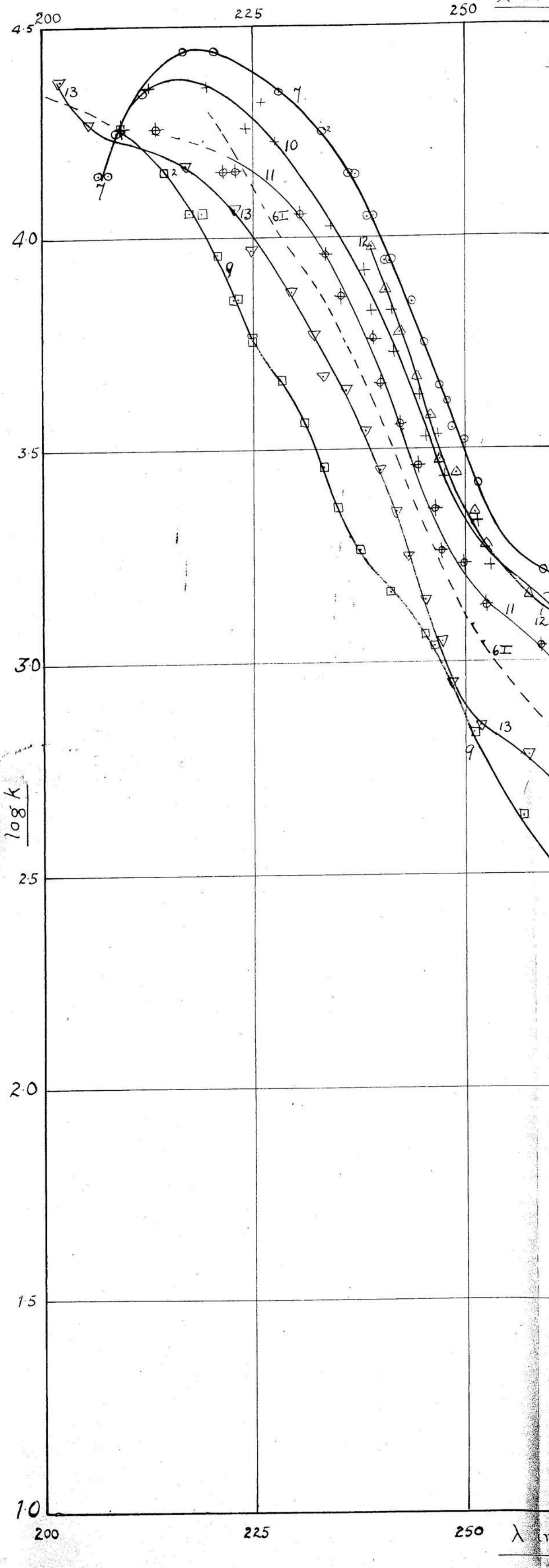
\+ SOLN. 10; $SnCl_2$ in KCl; $[Sn] = 0.0148$ m, $[KCl] = 3.624$ m
$[Cl^-]/[Sn] = 248.$

⊕ SOLN. 11; $SnCl_2$ in KCl+HCl; $[Sn] = 0.00553$ m, $[KCl] = 1.632$ m
$[HCl] = 0.520$ m, $[Cl^-]/[Sn] = 391$

▽ SOLN. 13; do. $[Sn] = 0.00214$ m, $[KCl] = 0.726$ m
$[HCl] = 0.340$ m, $[Cl^-]/[Sn] = 502$

△ SOLN. 12; $SnCl_2$ in KCl; $[Sn] = (0.00533)$ m, $[KCl] = 3.77$ m
$[Cl^-]/[Sn] = 739$

FOR COMPARISON, THE CURVE FOR SOLN. 6 (FIG. I) IS SHOWN (BROKEN LINE)



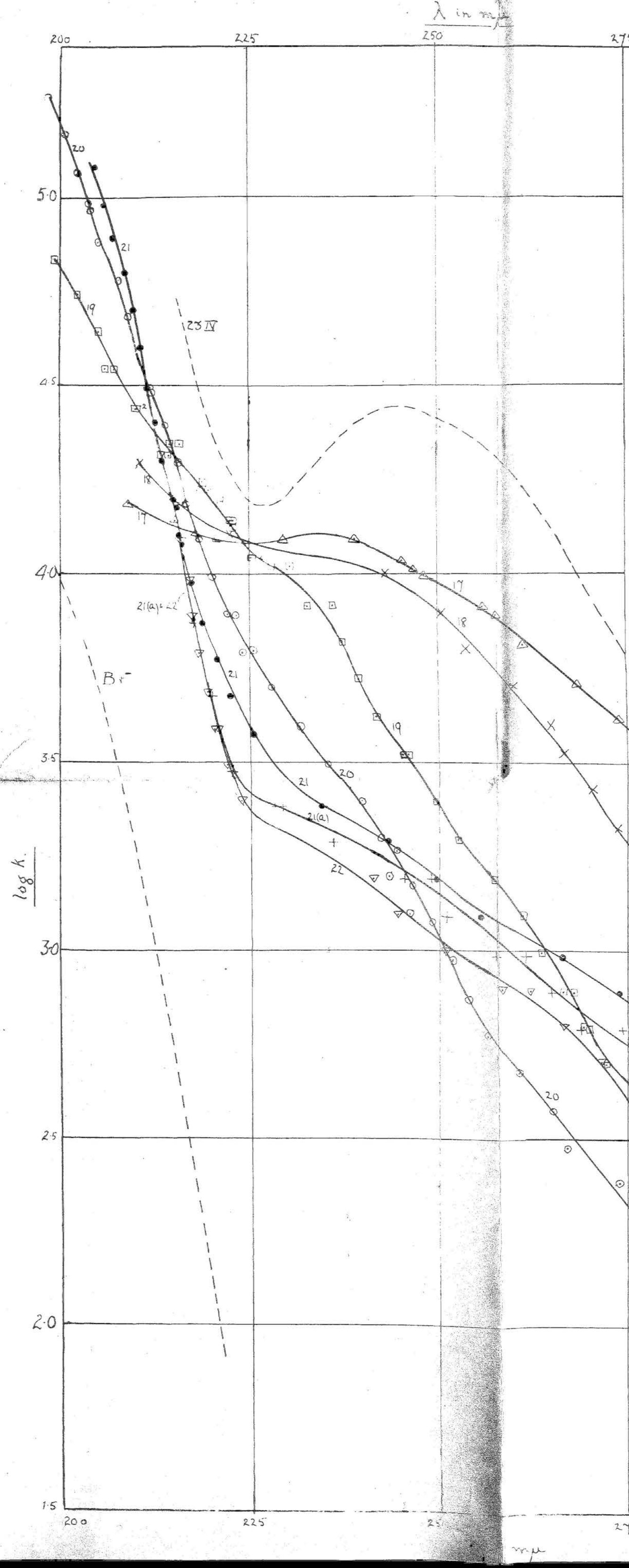


FIG. III. STANNOUS BROMIDE IN AQUEOUS SOLUTION:

SMALL EXCESS BROMION.

△ SOLN. 17. $SnBr_2$ in HBr; $[Sn] = 0.993$ mol/litre, $[HBr] = 1.54$ m. $\frac{[Br^-]}{[Sn]} = 3.53$.

× SOLN. 18. do. $[Sn] = 0.395$ m., $[HBr] = 0.946$ m., $\frac{[Br^-]}{[Sn]} = 4.41$.

⊡ SOLN. 19 do. $[Sn] = (0.080)$m, $[HBr] = 0.328$ m., $\frac{[Br^-]}{[Sn]} = (6.10)$

⊙ SOLN. 20 do. $[Sn] = (0.008)$m, $[HBr] = 0.159$m., $\frac{[Br^-]}{[Sn]} = (21.8)$

● SOLN. 21 do. $[Sn] = (0.0008)$m, $[HBr] = 0.0159$m

(20. DILUTED 1 : 10)

\+ SOLN. 21(a) AFTER STANDING 5 DAYS; SHOWING INCREASE OF HYDROLYSIS.

▽ SOLN. 22. do. $[Sn] = (0.00008)$m; $[HBr] = 0.00159$m

(20 DILUTED 1:100)

FOR COMPARISON, THE CURVE FOR SOLN 23 (FIG. IV) IS SHOWN (BROKEN LINE).

IN THIS FIG. THE ABSORPTION OF THE Br^- ION IS ALSO SHOWN.

FIG. IV. STANNOUS BROMIDE IN AQUEOUS SOLN. LARGE EXCESS BROMION.

× **SOLN. 23:** $SnBr_2$ in HBr ; [Sn] = 0·0981 mol/litre
[HBr] = 6·351 m ; $\frac{[Br^-]}{[Sn]} = 66·61$

□ **SOLN. 24:** DO. [Sn] = 0·0141 m
[HBr] = 1·349 m
$\frac{[Br^-]}{[Sn]} = 97·7$

▽ **SOLN. 25:** DO. [Sn] = 0·00322 m
[HBr] = 0·270 m
$\frac{[Br^-]}{[Sn]} = 85·4$

● **SOLN. 26:** $SnBr_2$ in KBr + HBr ; [Sn] = 0·0878 m
[HBr] = 0·099 m
[KBr] = 3·636 m
$\frac{[Br^-]}{[Sn]} = 44·8$

⊙ **SOLN. 28:** DO. [Sn] = (0·00878) m
SOLN. 26 DILUTED 1:10
[KBr] = 0·364 m
[HBr] = 0·010 m
$\frac{[Br^-]}{[Sn]} = (44·8)$

△ **SOLN. 29:** DO. [Sn] = 0·0173 m
[KBr] = 3·631 m
[HBr] = 0·544 m
$\frac{[Br^-]}{[Sn]} = 243$

⊕ **SOLN. 30:** DO. [Sn] = (0·00865) m
SOLN. 29 DILUTED 1:2
[KBr] = 1·816 m
[HBr] = 0·272 m
$\frac{[Br^-]}{[Sn]} = (243)$

log k

λ in mμ

FIG. V. STANNOUS IODIDE IN AQUEOUS SOLUTION.

- × Soln. 31. SnI_2 in KI; $[Sn]$ = 0·0175 mol/litre, $[I^-]$ = 2·785 m, $[I^-]/[Sn]$ = 159.
- △ Soln. 32. do. $[Sn]$ = 0·00279 m, $[I^-]$ = 1·320 m, $[I^-]/[Sn]$ = 487.
- \+ Soln. 33. do. $[Sn]$ = 0·00246 m, $[I^-]$ = 0·754 m, $[I^-]/[Sn]$ = 306.
- ● Soln. 34. do. $[Sn]$ = 0·00101 m, $[I^-]$ = 0·350 m, $[I^-]/[Sn]$ = 347.
- ⊡ Soln. 35. do. $[Sn]$ = 0·00043 m, $[I^-]$ = 0·276 m, $[I^-]/[Sn]$ = 638.
- ⊙ Soln. 36. do. $[Sn]$ = 0·000211 m, $[I^-]$ = 6·073 m, $[I^-]/[Sn]$ = 28770

THE DOTTED CURVES MARKED "31a", ETC., REPRESENT CURVES 31, 32, 33, ETC. ANALYSED ACCORDING TO THE METHOD GIVEN IN THE TEXT.

FOR COMPARISON ARE ALSO SHOWN:

(a) CURVE γII ($SnCl_2$ in 7·484 m HCl)

(b) " 23IV ($SnBr_2$ in 6·549 m HBr)

(c) THE THEORETICAL CURVE FOR THE DISPERSION OF LIGHT BY A TURBID MEDIUM (SEE TEXT) NUMBERED "37"

(d) THE ABSORPTION OF THE I^- ION.

λ in mμ

200 225 250 275 300 325

5·5 5·0 4·5 4·0 3·5 3·0 2·5

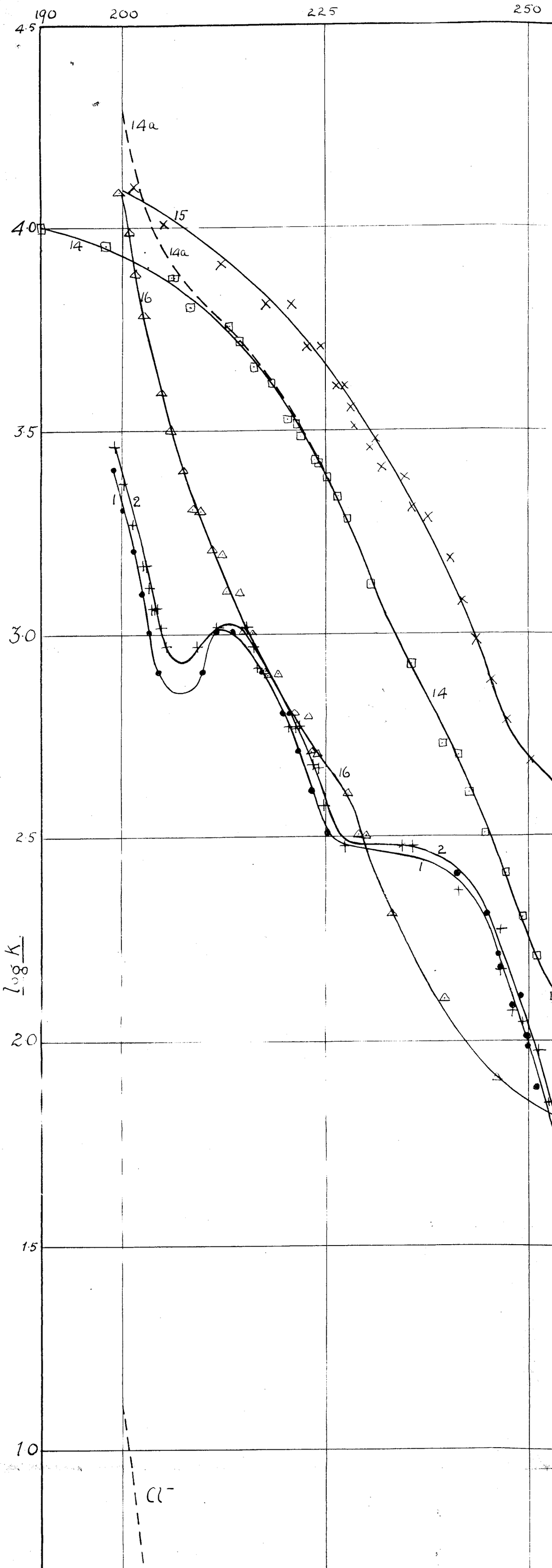


FIG. VI (a). STANNOUS PERCHLORATE IN PERCHLORIC ACID.
(b). K_2SnCl_6 IN AQUEOUS SOLUTION.

- SOLN. 1. $Sn(ClO_4)_2$ in 70% $HClO_4$; $[Sn] = 0.0977$ mol/litre, $[HClO_4] = ca.\ 8.4\,m$.
- \+ SOLN. 2 do. $[Sn] = 0.106\,m$.
- ⊡ SOLN. 14. K_2SnCl_6 in water ; concn. $= 0.612\,m$.
  CURVE 14a (SEE TEXT) IS SHOWN BY BROKEN LINE.
- × SOLN. 15. K_2SnCl_6 in HCl , $[Sn] = 0.00490\,m$, $[HCl] = 3.54\,m$
- △ SOLN. 16. do. $[Sn] = 0.000490\,m$
  15 DILUTED 1:10 $[HCl] = 0.354\,m$.

IN THIS FIG. THE ABSORPTION OF THE Cl^- ION IS SHOWN.

λ in mμ

log K

FIG. VII - TIN HALIDES, ETC., IN ALCOHOLIC SOLUTION.

- ⊙ Soln. 1. $SnCl_2$ in EtOH ; 0·00128 mols/litre.
- × " 2. do. ; 0·00064 m.
- ⊕ " 3. $SnBr_2$ in EtOH ; 0·00124 m.
- + " 4. do. ; 0·000496 m.
- ● " 5. SnI_2 in EtOH ; 0·000602 m.
- ⊙ " 6. do. ; 0·000339 m.
- × " 7. do. ; 0·0005668 m.
- △ 8. SnI_2 in 90% EtOH in Water ; 0·000301 m.
- ▲ " 9. SnI_4 in EtOH ; 0·000307 m.
- ⊡ " 10. SnI_4 in 75% EtOH in Water ; 0·000307 m.
- ▽ " 11. SnI_4 in 50% do. ; "
- ⊹ " 12. SnI_4 in 25% do. ; "
- ◆ " 13. Iodine in EtOH ; $[I_2] = 0·000804$ m.
- ◆ " 14. Iodine in aqueous KI soln. $[I_2] = 0·000201$ m. $[KI] = 0·0213$ m.